

**CONDITION OF SEDIMENTS IN SELECTED MARINAS
IN SAN FRANCISCO BAY: A PILOT STUDY**

Final Report

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Moss Landing Marine Laboratories

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SUMMARY

The San Francisco Bay Conservation and Development Commission (BCDC) and Moss Landing Marine Labs (MLML) designed a pilot study to investigate and evaluate the chemical state of water and sediment within San Francisco Bay marinas. The following report describes and evaluates environmental data collected from four recreational marinas: Berkeley Marina, Loch Lomond Marina, Ballena Isle Marina, and Corinthian Yacht Club, as well as a reference site at Paradise Cove. The intent of this work was to describe the chemical and physical conditions of the marinas so that the probability of ecological impacts resulting from marina activities could be assessed. Chemical analyses were performed using aliquots of homogenized sediment samples while water measurements were taken with water quality meters in the field and from grab samples collected at discrete water depths. A total of forty-three stations were sampled during the field survey, in August 2003. Chemical analyses were conducted through the fall of 2003 and the spring of 2004.

Summary of Results:

1. Sediment quality guidelines were useful in evaluating chemical pollution within the sediments of four San Francisco Bay marinas. Arsenic, chromium, copper, and zinc were most often found to exceed established Effects Range Low (ERL), Threshold Effects Levels (TEL) and Ambient guideline values. Use of these guidelines indicates that these chemicals pose a low, to occasionally moderate, probability of having associated acute toxic effects to aquatic life. Of these four metals, copper and chromium are of greatest concern. Long-term status and trend monitoring of these four trace metals in marinas is recommended.
2. Dissolved oxygen concentrations in Ballena Isle and Berkeley Marinas were low (<4 mg/l) in bottom waters at several locations and may present a risk of hypoxia to aquatic life. Additional monitoring of oxygen levels is recommended to improve both spatial and temporal resolution of oxygen saturation conditions.
3. Measured concentrations of cadmium, lead and polycyclic aromatic hydrocarbons (PAHs) were generally low and pose a low probability of having associated acute toxic effects to aquatic life.
4. Statistical analyses indicate Corinthian Yacht Club tended to have significantly lower metal concentrations than all other marinas, and was similar to the reference site at Paradise Cove. There was no clear pattern of statistical differences in metal or PAH concentrations among Berkeley, and Ballena Isle Marinas. Loch Lomond tended to have significantly lower PAH concentrations than most other marinas, though zinc was significantly greater there. Zinc was the metal most often seen to have significant differences between harbors and thus may be the metal most influenced by local uses. TOC and grain size showed no significant differences among the harbors.
5. PAHs were generally not correlated or were negatively correlated with metals, so their use or sources do not seem strongly linked. Copper, cadmium and zinc were often positively correlated suggesting common uses might be the source of these metals to the marinas. Arsenic did not correlate or was negatively correlated with the other metals indicating a separate use or source as compared to other trace metals.

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LIST OF ABBREVIATIONS

BPTCP	Bay Protection and Toxic Cleanup Program
CDFG	California Department of Fish and Game
COC	Chain of Custody
COR	Chain of Records
EMAP	Environmental Monitoring and Assessment Program
ERL	Effects Range Low
ERM	Effects Range Median
GC/ECD	Gas Chromatograph Electron Capture Detection
HCL	Hydrochloric Acid
HDPE	High-density Polyethylene
HMW PAH	High Molecular Weight Polycyclic Aromatic Hydrocarbons
LMW PAH	Low Molecular Weight Polycyclic Aromatic Hydrocarbons
MDL	Method Detection Limit
MLML	Moss Landing Marine Laboratories
MPSL	Marine Pollution Studies Laboratory
NOAA	National Oceanic and Atmospheric Administration
PAH	Polycyclic Aromatic Hydrocarbons
PCB	Polychlorinated Biphenyl
PEL	Probable Effects Level
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RWQCB	Regional Water Quality Control Board
SQC	Sediment Quality Criteria
SFBCDC	San Francisco Bay Conservation and Development Commission
TAC	Technical Advisory Committee
TEL	Threshold Effects Level
TOC	Total Organic Carbon
SWAMP	Surface Water Ambient Monitoring Program
USEPA	U.S. Environmental Protection Agency

Units

milliliter = 1 ml

microliter = 1 μ l

milligram = 1 mg

microgram = 1 μ g

nanogram = 1 ng

kilogram = 1 kg

1 part per thousand (ppt) = 1 mg/g

1 part per million (ppm) = 1 mg/kg, 1 μ g/g

1 part per billion (ppb) = 1 μ g/kg, 1 ng/g

INTRODUCTION

Ensuring that pollution is prevented and water and sediment quality is maintained is of concern to the San Francisco Bay Conservation and Development Commission (BCDC) in making permitting decisions on projects in and on the shoreline of San Francisco Bay. Marinas and recreational boating have been identified as a category of nonpoint source pollution in California by the State Water Resources Control Board (State Board) and the California Coastal Commission (CCC), and nationally, by the U.S. Environmental Protection Agency (U.S. EPA) and the National Oceanic and Atmospheric Administration (NOAA). However, few scientific studies have been conducted to determine whether, and to what extent, marina-related pollution is a problem in San Francisco Bay. BCDC has taken on this task as part of its nonpoint source pollution program, and this pilot study.

Marina and boating operations can be the source of pollutants such as heavy metals from boat hull paints, anti-corrodants, wood preservatives on docks and pilings, from various boat accessories such as chrome plating and stainless steel, and batteries; petroleum hydrocarbons (including PAHs) from fueling, oil spills, and fuel combustion from outboard motors and from creosote wood treatments in pilings and docks; and other pollutants discussed in Chapter Two, but not analyzed as part of this Pilot Study.

Many of the above pollutants can also originate from other non-marina sources such as municipal storm water discharges and discharges from industrial activities. This Pilot Study: Condition of Sediments in Selected Marinas in San Francisco Bay characterizes sediment quality conditions at four marinas, and isolates as much as possible marina-related pollution from other sources. Sediments samples were collected and analyzed as “surrogates” for water quality because of their ability to act as sinks for heavy metals and PAHs, and act as “long term integrators,” allowing for a single sampling event in each marina while representing conditions over a longer time period. Single event measurements of conventional water quality parameters in the water column (dissolved oxygen, temperature, salinity, pH and turbidity) were also taken to get a “snapshot” of general water quality conditions at the time of sampling. Benthic community samples were also taken and archived for future analysis (pending future funding).

Study Questions

BCDC staff and Moss Landing Marine Labs (MLML) developed the following study questions, with input from the marina study’s Technical Advisory Committee (TAC)¹ and the San Francisco Bay Marinas and Recreational Boating Nonpoint Source Task Force (Task Force).²

¹ A group comprised of scientists from the San Francisco Regional Water Quality Control Board (San Francisco Regional Board), California State Water Resources Control Board (State Board), San Francisco Estuary Institute (SFEI), NOAA CSC, California Coastal Commission (CCC), Moss Landing Marine Labs (MLML), and representatives from Recreational Boaters of California (RBOC) and the California Association of Harbor Masters and Port Captains.

² A group comprised of marina and boating operators and associations, environmental organizations, and local, state and federal government organizations (Appendix B lists the major active organizations on the Task Force).

1. “What is the sediment chemistry concentration in four recreational marinas in San Francisco Bay in regards to the following pollutants associated with marina and recreational boating operations: trace metals (copper, zinc, chromium, lead, arsenic, cadmium), polycyclic aromatic hydrocarbons (PAHs)?”
2. “Do sediment chemical concentration levels meet or exceed sediment guidelines (e.g. Effects Range Low [ERL], Effects Range Median [ERM], Threshold Effects Level [TEL], and Probable Effects Level [PEL])?”
3. How do sediment concentration levels compare to Ambient sediment concentrations calculated for the Bay, and Regional Monitoring Program (RMP) reference stations at Paradise Cove?”
4. “What general water quality conditions exist in the four marinas in regards to dissolved oxygen, temperature, turbidity, pH, and salinity?”
5. “Is there a noticeable difference in contaminant levels found between the four marinas sampled and can we make plausible inferences as to why those differences exist?”

Study Area

Marina Selection Procedure. BCDC staff developed marina selection criteria for the pilot study in conjunction with the Task Force and the TAC. Because the pilot study involved only four marinas due to budget constraints, selecting these marinas carefully was crucial to best answer the research questions, and to the maximum extent practicable, to be representative of the wide variety of marinas in San Francisco Bay. It is difficult to define a typical marina in San Francisco Bay, because of their wide variety of physical, geographical, environmental, and demographical characteristics. BCDC staff developed a marina matrix for forty-three marinas, which aided in this process. The matrix included the following data for each marina (see Appendix C for the condensed marina selection matrix used by the TAC):

1. Marina size (number of berths)
2. Boat types
3. Marina age
4. Activity level (vessel traffic)
5. Surrounding land-use
6. Historical land-use
7. Current and flushing patterns
8. Marina layout (e.g. open or enclosed)
9. Water depth
10. Sediment depositional rates
11. Sediment depositional patterns
12. Dredging frequency
13. Storm water influence (e.g. municipal storm drain or no municipal storm drain)
14. Marina facilities
15. Environmental services/policies

BCDC staff obtained this data from a variety of sources, including a telephone survey of marina harbormasters, the California Department of Boating and Waterways (DBW) databases,

the California Coastal Commission Boating Clean and Green Campaign's databases, task force members, and marina site visits.

The data collected revealed that several marinas in San Francisco Bay contain municipal stormdrain outfalls that may discharge municipal stormwater and dry weather flows into the marina basins. These marinas were automatically disqualified from the Pilot Study in order to isolate the pilot sites from non-marina and recreational boating-related sources of nonpoint pollution.

In order to represent the different types of marinas in San Francisco Bay, the remaining marinas were categorized on a scale of 1-4, based on their available facilities and services. Marinas near the top of the scale (#4) were those marinas with a variety of services such as a fuel dock, maintenance areas, haul-out facilities, dry storage, launch ramps, and shore side car parking lots. Marinas on the bottom of the scale (#1) were those marinas with few of those services. After categorization, the following criteria were used to select the most appropriate marinas for the study. Since it is difficult to find four marinas that fit all the criteria perfectly, the criteria were prioritized according to what would affect the results the most.

1. To the best extent practicable, all four marinas will be located beyond the influence of municipal storm drains to minimize the intervening variables associated with nonpoint source pollution from municipal stormwater.
2. To the best extent practicable, the surrounding land-use of all four selected marinas will have low industrial activity to minimize intervening variables associated with nonpoint source pollution from these activities.
3. To the best extent practicable, all four marinas will have similar sediment depositional rates.
4. To the best extent practicable, all four marinas will have roughly the same proportion of 'types' of boats, including sailboats, powerboats, and liveaboards.
5. To the best extent practicable, all four marinas will have roughly the same level of vessel traffic, preferably busier marinas, rather than marinas with boats sitting in slips most of the time.
6. To the best extent practicable, all four marinas will be roughly the same age.
7. To the best extent practicable, all four marinas will be roughly the same depth at Mean Lower Low Water (MLLW).

The selection process resulted in the identification of four suitable marinas and one reference location (Figure 1): Ballena Isle Marina (Alameda), Berkeley Marina, Corinthian Yacht Club (Tiburon), and Loch Lomond Marina (near Richmond/San Rafael). A reference location was selected at Paradise Cove (reference) for comparison to previous surveys and ambient conditions. This survey was intended to give a broad assessment of chemical conditions throughout the four San Francisco Bay marinas by providing multiple analyses from the water column and from sediment samples.

Table 1. Selected Marinas³

Marina	Location	Size	Facilities	Category
Berkeley Marina	City of Berkeley, Alameda County	1100 wet berths 77 dry storage	fuel dock, full service boat yard, boat launch, dry storage, parking lot	4
Loch Lomond Marina	San Rafael, Marin County	517 wet berths 250 dry storage	fuel dock, mechanic shop, boat launch, parking lot	3
Ballena Isle Marina	City of Alameda, Alameda County	504 wet berths 45 dry storage	fuel dock, hoist, parking lot	2
Corinthian Yacht Club	Tiburon, Marin County	85 wet berths 25 dry storage (+40 dinghy racks)	hoist, small maintenance area, parking lot	1

³ See Appendix D for additional information on the selection criteria for each marina

BERKELEY MARINA

Berkeley marina is located on a man-made peninsula on the Western edge of the City of Berkeley, Alameda County, in central east San Francisco Bay, four miles north of the San Francisco Bay Bridge (see Figure 1).

Category. On BCDC's marina scale, Berkeley is categorized as a level four marina. The largest marina in Northern California, Berkeley marina has 1100 berths and can accommodate vessels up to 135 feet long. Available facilities include a fuel dock, a boat yard with haul-out capacity and scraping and sanding services (also a marine canvas business), a public boat launch, a seventy-seven boat capacity dry storage area, a public fishing pier (on open water outside the marina basin), charter fishing boats, and public parking lots. Other marina-related businesses on the marina premises include several restrooms and showers, a yacht club, hotel, restaurants, and a day cruise business (Hornblower), playgrounds, and a marina sports center.

Layout and Structures. The general layout of the marina is an enclosed basin, with an entrance opening flanked by an entrance breakwater, which helps to eliminate surge and rough water. Boat docks are supported with wood pilings and to a lesser extent, concrete pilings. Wood pilings are mostly treated with copper based wood preservatives, while some are treated with creosote (see Chapter Three for a description of these preservatives).

Surrounding Land Use. Berkeley's surrounding land and water-uses include several acres of public parks (including Cesar Chavez Park and Shorebird Park), an adventure playground, a nature center, and the South Sailing Basin with a beach and rocky shore, and a small boat dock and hoist. Just off the marina peninsula along the Bay shoreline is Interstate Highway 80, and City of Berkeley public beaches.

Boat Types and Activity. The marina hosts a wide diversity of vessels, consisting of 80 percent sailing and 20 percent power boats. A few houseboats occupy docks on the East shore. Slips vary in size, with the shortest being eighteen feet, and the longest at eighty-five feet. Approximately 10 percent of recreational boats are marina authorized liveaboards.⁴ In addition to recreational vessels, the marina also hosts public fishing charter boats, and large 'Hornblower' dinner cruise boats. A research and marine educational vessel also docks at the marina. The harbormaster describes the marina as fairly busy, especially on weekends when 75 percent of boaters are there, and there is foot traffic from sailing and yacht club clients.

History. The marina was first constructed in 1936, and expanded several times in the 1960s, '70s, and '90s. During World War II the marina was used as a landing barge training base operated by the Navy. For several years, the marina co-existed with a city landfill just to the Northeast, which is now covered by Cesar Chavez Park. The landfill began receiving waste in

⁴ Live-aboard boats are designed and used for active navigation but are distinguished from other navigable boats in that they are also used as a primary place of residence. See BCDC. 2003. San Francisco Bay Plan. San Francisco Bay Conservation and Development Commission (BCDC). San Francisco. Reprinted March 2003, p. 49. See also California Code of Regulations Title 14. § 10128. "A 'live-aboard' boat is a boat that is not a transient boat, that is capable of being used for active self-propelled navigation, and that is occupied as a residence as that term is defined in California Government Code Section 244."

1961 and concluded operations in 1983, after which it underwent formal closure, and is currently conducting post-closure operations and maintenance (SCS Engineers 2003). An operational methane burner still exists on site, and the site's groundwater and storm water is monitored periodically by the City of Berkeley.

Sediment Deposition. Berkeley Marina has an average water depth of twelve feet at mean lower low water (MLLW), and an entrance depth of eight feet (MLLW). It has not been dredged since 1989. The North entrance is currently in need of dredging. According to information from Emery Cove Yacht Harbor next door, sediment deposition rates are about 2.4 inches per year.

Environmental Services and Policies. The marina has a variety of environmental services, and conducts some environmental management practices. Services include a sewage pump out station, used oil collection, and absorbent pad distribution and collection facilities. Additionally, the marina has several ordinances in its tenant lease that apply to environmental issues, which are summarized below. Dilapidated, unseaworthy boats are prohibited in the harbor. Dock boxes are prohibited to contain flammable liquids or hazardous materials. All discharges of any material are prohibited in the harbor, including oil, spirits, flammable liquids, contaminated bilge water, treated or untreated sewage, grey water, and solid and hazardous waste. Garbage must be deposited in receptacles provided by the marina. Additionally, docks must be kept free and clear of hazardous or flammable materials. While repairs and maintenance of vessels are allowed in berths, no debris or fluids from this activity are allowed to accumulate on the docks or enter marina waters. Welding equipment, burning torches, spray paint and sand blasting equipment is prohibited except in specifically designated areas. The use of boat sanitary facilities is prohibited while docked in the marina, except in vessels that are equipped with an approved operating device for the containment of sewage and gray water. Fish cleaning is prohibited in the marina except in designated areas. The boatyard, which is a separately owned business, conducts wet sanding and has a waste water filtration system (this is regulated under a National Pollution Discharge Elimination System [NPDES] permit, administered through the San Francisco Regional Board).

Non-BCDC Water Quality Data. Some water quality monitoring has been conducted in Berkeley Marina. The City of Berkeley (Environmental Health Department) monitors for bacteria (fecal coliform and *E. coli*) in the marina and its adjacent shorelines, in a proactive effort to safeguard public health in this large public recreation area. While some problems have occurred on the North and South Shorelines (outside the marina basin) and within the sailing basin, it is difficult to ascertain clear trends or problems using monthly data. While BCDC did not sample for bacteria in its pilot study, WaterKeepers Northern California/San Francisco BayKeeper will include this marina as part of its bacteria monitoring program, and the information obtained will help inform BCDC's marina program.

SCS Engineers, a consultant for the City of Berkeley Public Works Engineering Department periodically monitors the groundwater and surface stormwater of Cesar Chavez Park, the former landfill located adjacent to and Northeast of Berkeley Marina. Although these measurements were not taken within the marina basin and were not factored into the sediment analysis, the data are presented here for the reader's reference. In August 1994 samples taken from levee seepage wells, leachate wells, and groundwater monitoring wells were analyzed for total dissolved solids

(TDS), chemical oxygen demand (COD), chloride, chromium, lead, and volatile organic compounds (VOC), and volatile aromatic hydrocarbons (using EPA Method 8240). Five shallow ground water monitoring wells were sampled. TDS concentration for ground water samples ranged from 3,200 to 23,000 mg/l. Chloride concentrations ranged from 3,600 to 14,000 mg/l. Lead was not detected in any of the samples. Chromium was detected in samples from three of the wells at concentrations ranging from 0.031 to 0.064 mg/l. Chromium concentration was above the drinking water MCL of 0.050 mg/l in samples from two of the wells. VOCs were not detected in any of the five ground water wells sampled. In leachate wells, TDS concentrations ranged from 2,000 to 7,800 mg/l. Chloride concentrations ranged from 500 to 1,700 mg/l. Lead was not detected in any of the leachate wells. Chromium was detected in two of the wells, one of which had a concentration slightly above the MCL of 0.05 MG/L (L-7, 0.059 mg/l). Low concentrations of volatile aromatic hydrocarbons were detected in samples from two wells (L-6 and L-7). Benzene was detected in well L-6 at a concentration of 1.4 µ/l. In levee seepage wells, TDS concentrations ranged from 1,300 mg/l to greater than 5,300 mg/l. Chloride concentrations ranged from 54 to 5,300 mg/l. Lead was not detected in any of the samples. Chromium was detected in samples from three of the wells at concentrations ranging from 0.013 to 0.023 mg/l which are all below the MCL of 0.050 mg/l. Volatile aromatic hydrocarbons were detected in one of the wells (G-5). Benzene was detected at a concentration of 2.7 µ/l which is slightly higher than its MCL of 1.0 µ/l (SCS Engineers, 1994). Selected chemical analysis results were reviewed for general correlation to observed measures in the current marina Pilot Study.

LOCH LOMOND MARINA

Loch Lomond Marina is located in Central San Rafael, Marin County, in San Pablo Bay just northwest of San Rafael Canal (Figure 1).

Category. On the marina scale Loch Lomond is categorized as a level three marina. It has 517 wet berths and a 250 boat capacity dry storage area (one half of which is slated for condo conversion), and parking lots. Other facilities include a fuel dock, a maintenance area for boat engine work, public boat launch ramp, some covered slips, and a bait shop located on the fuel dock. Additional supporting facilities include restrooms, showers, a restaurant, and a yacht club.

Layout and Structures. The general marina layout is a rectangular shaped enclosed basin, flanked by a manmade breakwater of vegetated rip rap on the East and South sides, which also serves as a pedestrian pathway. The marina was constructed by filling in mudflats and then dredging out the basin. A recent upgrade of the marina was conducted in 1995 replacing several docks. Currently marina structures are wood docks supported by creosote treated wood pilings (see Chapter Three for a description of this wood preservative).

Surrounding Land Use and History. Loch Lomond's surrounding land-use is mainly residential, especially in the surrounding hills. The marina property contains a commercial strip mall with a dry cleaning and laundry facility. Before the marina was constructed in 1958, the marina basin site was characterized by mud flats.

Boat Types and Activity. According to its harbormaster, Loch Lomond is a very busy marina, especially on weekends. Approximately sixty percent of Loch Lomond's boats are

power boats, and the remaining forty percent are sailboats. Slips accommodate boats as small as twenty-four feet and as long as sixty-two and a half feet. Ten percent of all boats are marina authorized liveaboards.

Sediment Deposition. The marina basin has an average water depth of seven feet and eight feet at the entrance. Sediment depositional rates are fairly rapid with 0.5 – 1 feet filling in per year, requiring frequent maintenance dredging episodes. Depositional patterns are uneven however, with the west basin filling in faster than the east basin, according to the harbormaster. Before the last dredging episode in April 2003 depths in the channel ranged from –3.5 to –6.0 feet MLLW, and depths around the berths ranged from –3.0 to –8.0 MLLW (ABT 2001). Prior to this episode, it hadn't been dredged for at least five years. The east basin was last dredged five years ago.⁵

Environmental Services and Policies. Environmental services at the marina include a sewage pumpout station located on the fuel dock, used oil recycling, and an absorbent pad exchange program. The marina also has some rules and regulations for its tenants that apply to environmental issues. No fueling is allowed at any place other than the fuel dock. Petroleum, paint products, and batteries are prohibited from being stored in dock areas. Fish cleaning and preparation of bait are also prohibited in the dock areas. Repairing or servicing of automobiles is prohibited at the marina, and oils and oil filters from vessels are prohibited from being dumped in garbage bins. These items are required to be disposed of in recycling areas. Unseaworthy, dilapidated, badly deteriorated, or inoperable vessels are not permitted to be stored in the harbor.⁶ The marina office also provides free clean boating literature.

Non-BCDC Water Quality Data. There is no active water quality monitoring program at Loch Lomond marina. However, in 2001 the marina conducted tier three testing of bottom sediments in preparation for maintenance dredging. This information provided background data to help inform BCDC's pilot study. This testing was conducted in accordance with requirements from the Dredged Materials Management Office (DMMO), a collaboration of regulatory agencies for dredging (U.S. Army Corps of Engineers, U.S. EPA, SF Regional Water Quality Control Board, and BCDC). Analytical chemistry, bioassay testing (water column and benthic), and grain size analysis were conducted on sediments from Loch Lomond. Samples were collected and composited in February 2001 at seven sites around the entrance channel and berth areas. Sample cores were taken at depths of the anticipated dredge (-10 feet MLLW). Selected chemical analysis results were reviewed for general correlation to observed measures in the current marina Pilot Study.

BALLENA ISLE MARINA

Ballena Isle Marina is located in Central San Francisco Bay in an enclosed basin on the south side of Alameda Island. While most Alameda marinas are located on the north side, in the

⁵ Personal communication with Pat Lopez, Loch Lomond harbormaster, 6/03

⁶ Loch Lomond Marina Berth Rental Agreement and Rules and Regulations

Oakland Estuary, Ballena Isle is located in San Francisco Bay, and is isolated from the other marinas (Figure 1).

Category. Ballena Isle is categorized as a level two marina on BCDC's marina scale. It has 504 berths, and a forty-five boat capacity dry storage area. Available facilities include a fuel dock, a hoist for hauling out boats, and parking lots. Additional supporting facilities include restrooms and showers, a yacht club, restaurant, a convenience store, and laundry.

Layout and Structures. Ballena Isle is a horseshoe shaped enclosed-basin marina built between land and a man made peninsula, made from dredged material. There is a small breakwater made from rip rap at the Southeast end. Docks are supported by wood pilings treated with creosote and copper based wood preservatives (see Chapter Three for a description of these wood preservatives).

Surrounding Land Use and History. The marina's surrounding land-use is mostly residential and open space. One unique aspect of Ballena Isle is that it is located next to several waterfront condos with private boat slips (located in Ballena Bay channel). Historically, the marina's surrounding area was owned by the federal government, and was kept as open space.

Boat Types. Sixty-five percent of the boats docked in the marina are sailboats, and thirty-five percent are power. Slips accommodate boats from twenty-four to seventy feet. The marina allows 10 percent of its tenants to be liveaboards.

Sediment Deposition. The average depth of the marina basin and the entrance is eight feet at MLLW and the entrance is eight feet at MLLW. Based on a 2001 bathymetric survey, the marina receives approximately six inches per year of sediment deposition. The marina was last dredged in April 2002, when approximately 27,000 cubic yards of sediment were removed from the main fairway and the rest of the marina area.⁷ The marina needs to be dredged approximately every seven years, although the harbormaster predicts it will need to be dredged in two years time, sooner than usually predicted. This could be due to strong currents, and the fact that new sand was added to the nearby Crab Cove Beach.

Environmental Services and Policies. Environmental services at the marina include a sewage pumpout, absorbent pad distribution and collection, and waste oil collection. The marina also has some terms of mooring and rules and regulations that apply to environmental issues. Any unnecessary operation of engines is not permitted. Tenants must agree not to do major boat repairs, such as motor overhauls, hull painting and structural changes, to their boats while in the marina. Dock areas must be kept free of non-marina approved materials. Boaters are prohibited from introducing hazardous wastes into marina waters or adjoining property. Boats are prohibited from being fueled anywhere except at the fuel dock. Waste oils, paint solvents, paints and other chemicals must be disposed of in receptacles specifically provided by the marina. Fishing and swimming are not permitted within the marina. Open fires or barbecues are not permitted on docks, but gas fired barbecues are permitted on boats only. Pets must be leashed at

⁷ BCDC permit no. 12-84, amendment #4, dredge quantity computations by Sea Surveyor, Inc. maximum amount authorized in permit 50,000 cubic yards until 2006

all times, and pet owners are responsible for cleaning up pet feces. Lastly, marine sanitation devices must be emptied at the designated discharge facility (pumpout).

Non-BCDC Water Quality Data. There is no active water quality monitoring program at Ballena Isle Marina. However, bottom sediments were sampled and analyzed in preparation for maintenance dredging and disposal in August 1998. This information provides background data to inform BCDC's pilot study. Advanced Biological Testing, Inc. (ABT) conducted chemical, physical, and bioassay testing of sediments at Ballena Isle by under guidelines established in PN 93-2 (ACOE et al 1992) as well as guidelines provided in the Testing Manual for the Evaluation of Dredged Material Proposed for Ocean Disposal (U.S. EPA/ACOE, 1991). The marina was divided into three dredging sections, and one composite sample comprised of five sediment cores was tested per site, for a total of three composite samples. Each core sample was taken to a maintained depth of -10 feet MLLW. Selected chemical analysis results were reviewed for general correlation to observed measures in the current marina Pilot Study.

CORINTHIAN YACHT CLUB

Corinthian Yacht Club is a private 'members-only' marina in Tiburon, Marin County. The marina is located on the north-western side of Raccoon Straits between Corinthian and Belvedere Islands in the west, and the Tiburon / San Francisco - and Angel Island - Ferry docks to the east (Figure 1).

Category. On BCDC's marina scale, Corinthian is categorized as a category one marina. It has approximately eighty-five boats in wet slips, and a 25-boat capacity dry storage area, where members also conduct maintenance work adjacent to the water's edge. Additionally, the club has forty dinghy racks under the clubhouse for Zodiacs and small dinghies. The only other available facilities are a launch hoist and parking lot.

Layout and Structures. A manmade breakwater on the southeast side gives the marina a fish hook shape and encloses Corinthian's basin. Its docks are supported by plastic coated steel pipe pilings, and twenty-five pilings are made of creosote treated wood (See Chapter Three for a description of this wood preservative).

Surrounding Land Use. The surrounding land uses at Corinthian are commercial and residential, with several shops and restaurants flanking Tiburon's main street and the Bay's shoreline just northeast of the marina basin.

Boat Types and Activity. Sixty-six percent of Corinthian's boats are sailboats, with the remaining thirty-four percent power. While weekday boat traffic is low in the marina, the weekends are quite busy, with thirty-five of its boats in use, as well as guest boaters going to nearby cafés and restaurants.

History. Corinthian is a relatively old marina. Anchorage and moorings were created in 1887, and the marina has slowly expanded since then. The historical use near the site included a terminal and railhead for the Pacific Northern Railroad Ferry, connecting to San Francisco's docks and the Pacific Northwest.

Sediment Deposition. Corinthian's water depth varies, ranging from 4.7 feet in section G (in the center of the basin) to 9.7 feet near the breakwater (east to southeast end of the basin). The channel entrance depth is 12.5 feet. Sediment deposits at an approximate rate of five to six inches per year, in an uneven pattern. The northwest end of the basin has experienced more silting than other areas. Corinthian was last dredged in 1998, and approximately 31,000 cubic yards of sediment was removed.⁸ The marina is on a six-year dredging cycle and currently in need of dredging. Marina officials are proposing to dredge approximately 48,800 cubic yards over the next ten years.⁹

Environmental Services. This small marina does not have any extensive environmental services, such as sewage pumpouts or used oil collection and recycling. The harbor has several binding rules and regulations that apply to environmental issues, however. No discharge of marine toilets or contaminated bilge water is permitted in the marina basin. Boats in berths are prohibited from continuously running their engines. Liveaboards are prohibited. Solid and hazardous wastes must be disposed of in specific containers provided by the club, or permanently removed from the premises. Storage of flammable materials are not permitted in lock boxes, and major repair, rebuilding or remodeling work is not permitted in the harbor. Minor repair in the harbor is permitted, but rules state that it must be performed in an environmentally sound way (no specific practices are listed in the rules and regulations document). Finally, unseaworthy boats are not permitted to be berthed in the harbor.¹⁰

Non-BCDC Water Quality Data. Like most marinas in San Francisco Bay Corinthian does not regularly test marina waters or sediments. Corinthian conducted sediment sampling in preparation for maintenance dredging and disposal activities in 2003, however. Chemical and physical analyses of sediments were conducted, as well as biological testing (bioassays). Sediment core samples were collected from eight stations within the harbor. Four sample stations were assigned to each of the two designated sample areas within the harbor. Individual core samples were composited in the laboratory to form one representative sample per area. Test results were evaluated to assess the suitability of the harbor's dredged material for the in-Bay sediment disposal site located at the Alcatraz Environs (SF-11). Analytical methods followed procedures specified in: *Evaluation of Dredged Material Proposed for Discharge in Waters of the U.S. – Testing Manual* (ITM; USEPA/ACE 1998) and *Guidelines for Implementing the Inland Testing Manual in the San Francisco Bay Region* (PN 01-01; USACE 2001). Selected chemical analysis results were reviewed for general correlation to observed measures in the current marina Pilot Study.

⁸ Ingo Schreiber, per. com., 11/03

⁹ BCDC permit application M81-67 amendment #1

¹⁰ Corinthian Yacht Club Harbor Rules and Regulations. As amended December 2002.

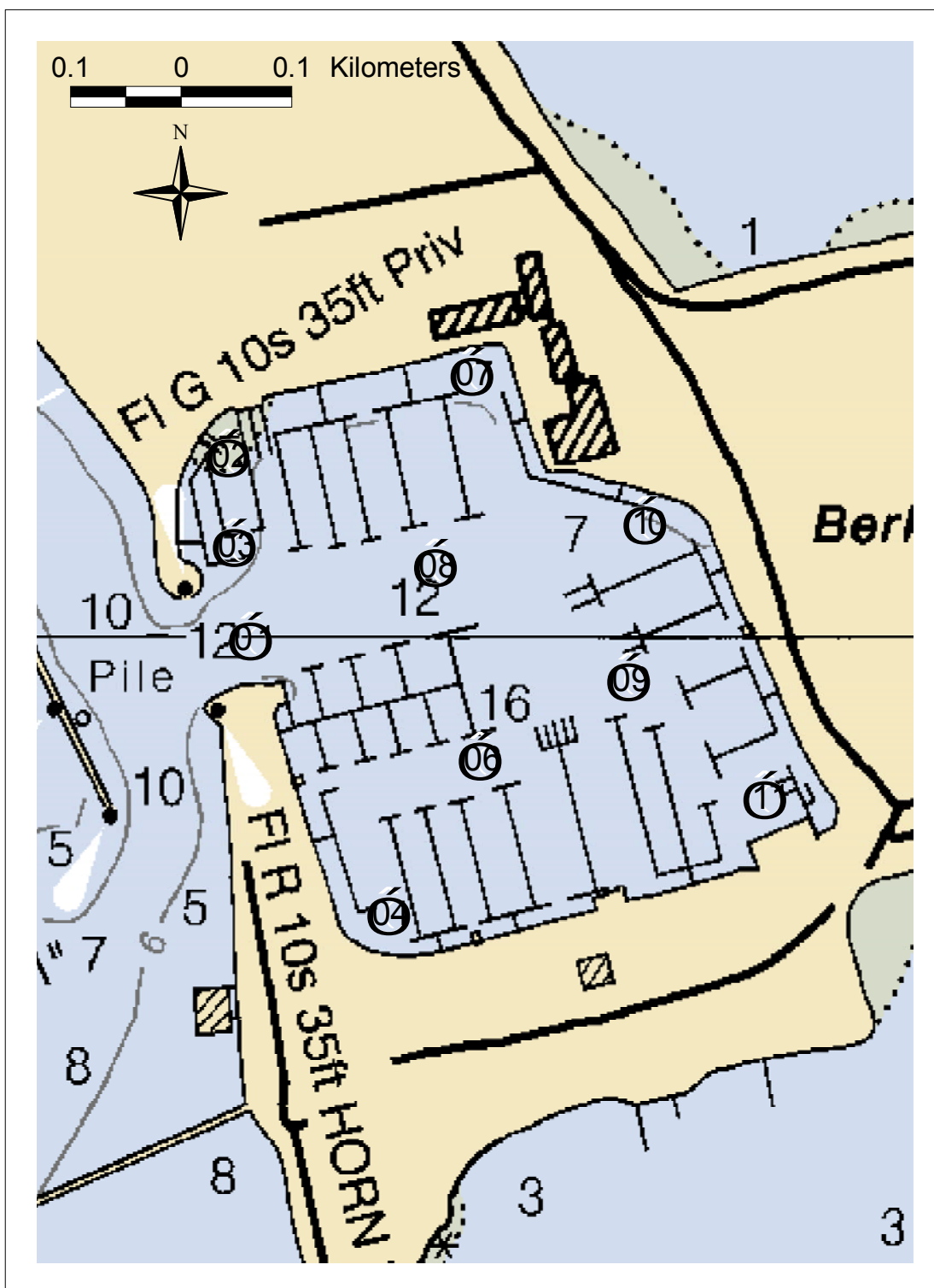


Figure 2a. San Francisco Bay Marina Sampling Locations-Berkeley Marina

*Sample #5 is not shown because it is a blind field duplicate taken at station #8

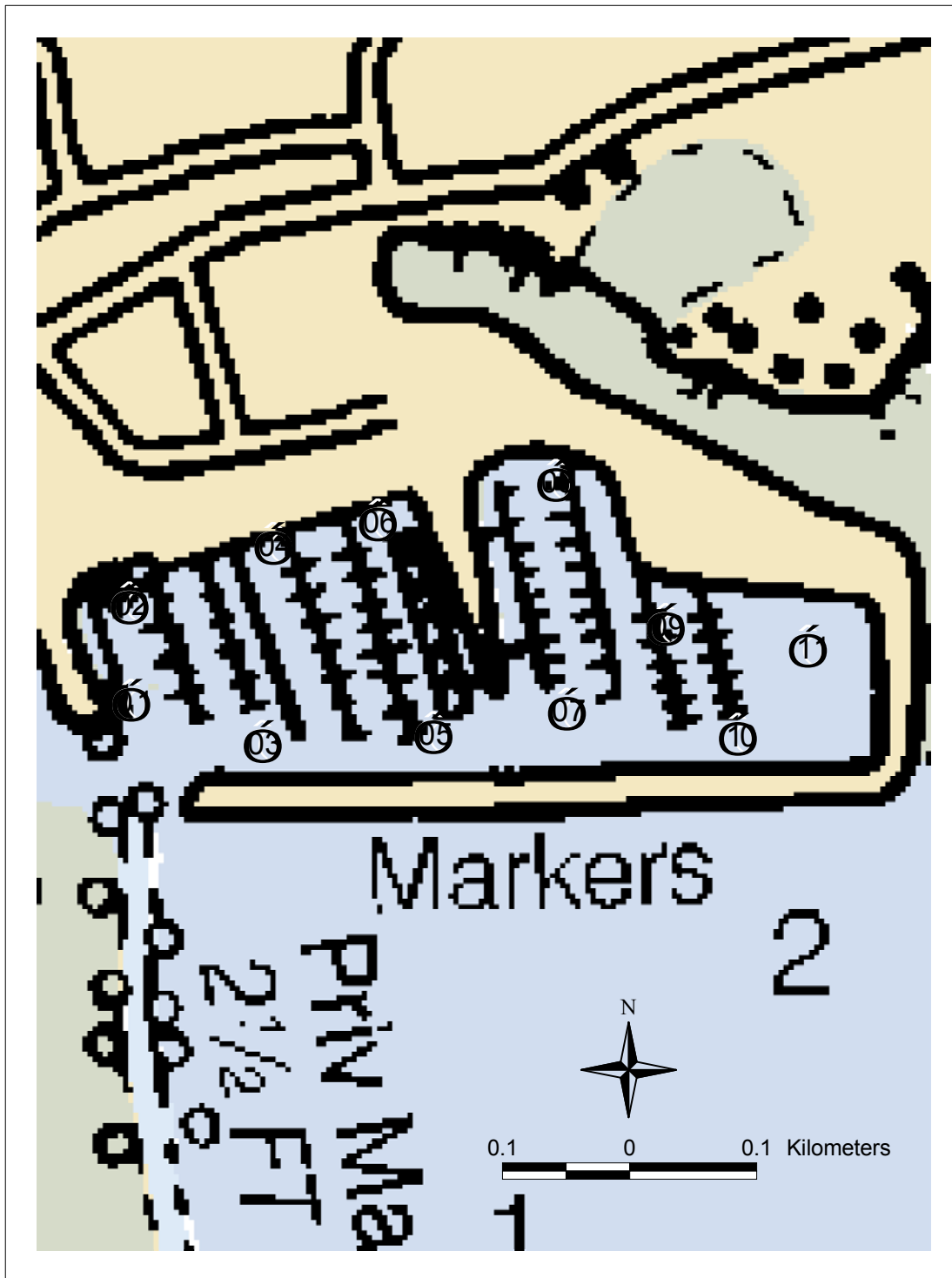


Figure 2b. San Francisco Bay Marina Sampling Locations-Loch Lomond Marina

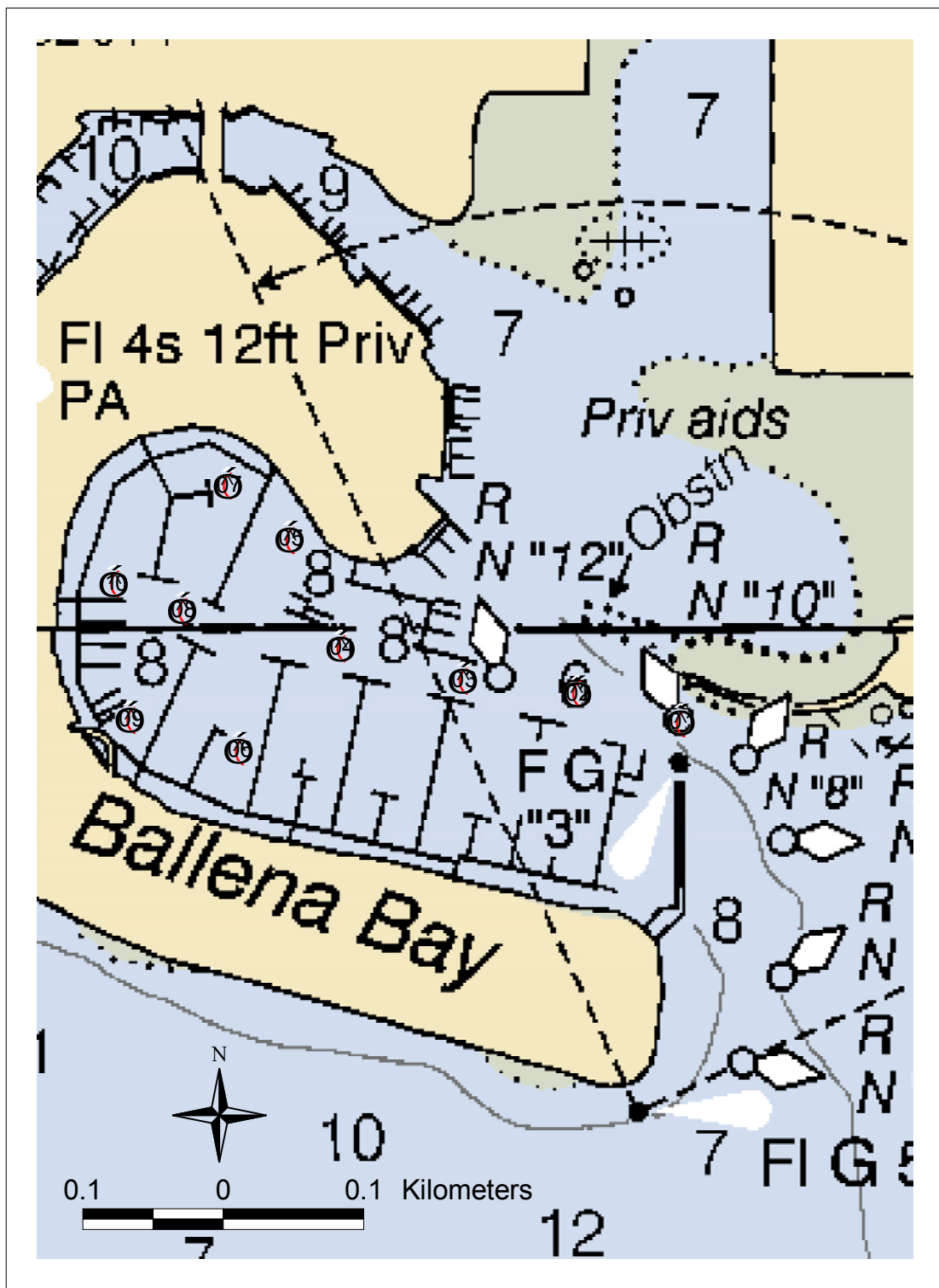


Figure 2c. San Francisco Bay Marina Sampling Locations-Ballena Isle Marina



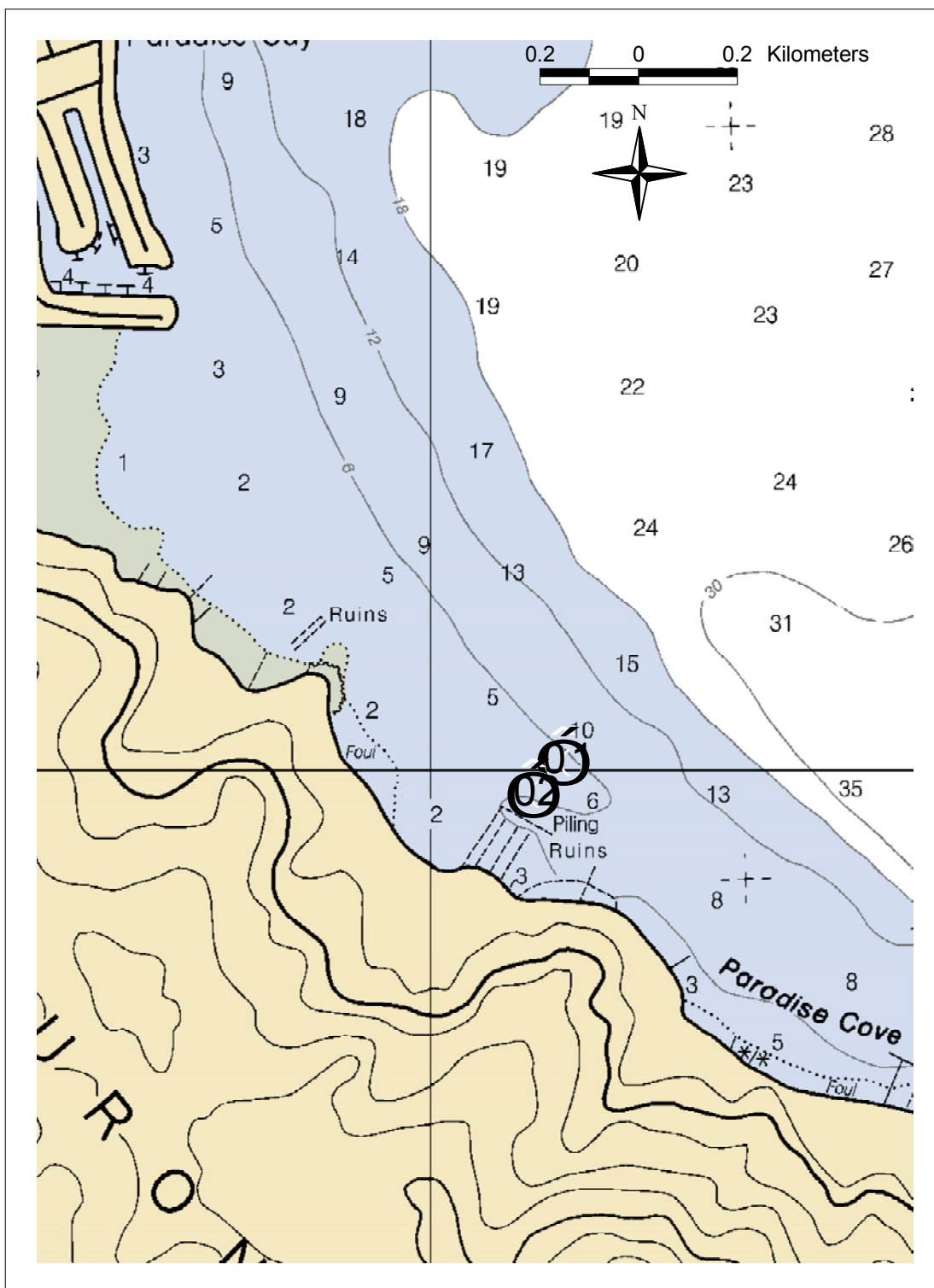


Figure 2e. San Francisco Bay Reference Sampling Locations-Paradise Cove
 *Sample #3 not shown because it's a blind field duplicate taken at station #1

METHODS

Sampling Design

A directed point sampling design was required to address the need to identify potential areas of concern within marinas. Station locations (latitude & longitude) were predetermined by agreement with Moss Landing Marine Labs (MLML) and BCDC staff, as well as the Technical Advisory Committee (TAC). The intent of the survey and sample locations was to give a broad assessment of chemical conditions throughout the four San Francisco Bay marinas by providing multiple chemical analyses from sediment samples and single event measurements of conventional water quality parameters. A total of forty-one stations and two field duplicate stations within the four harbors and the Paradise Cove reference site were sampled August 26-27, 2003 (Figures 2 a-e). Sample locations were chosen along a gradient from the front entrance to the back of each marina, with several samples along the channels and fairways of each marina (See figures 2a-e). Water column profiles were conducted at each station to provide discrete measures of salinity, temperature, pH, turbidity, and dissolved oxygen at three depths. Sediment samples were collected and analyzed for grain size, total organic carbon, trace metals, and trace organics.

Sample Collection and Processing

Summary of Methods

Specific techniques used for collecting and processing samples are described in this section. Because collection of sediments influences the results of all subsequent laboratory and data analyses, it was important that samples be collected in a consistent and conventionally acceptable manner. Field and laboratory technicians were trained to conduct a wide variety of activities using standardized protocols to ensure comparability in sample collection among crews and across geographic areas. Sampling protocols in the field followed the accepted procedures of BPTCP, EMAP, and SWAMP, which included methods to avoid cross-contamination; methods to avoid contamination by the sampling activities, crew, and vessel; collection of representative samples of the target surficial sediments; careful temperature control, homogenization and subsampling; and chain of custody procedures.

Cleaning Procedures

All sampling equipment (i.e., containers, container liners, scoops, water collection bottles) was made from non-contaminating materials and was precleaned and packaged protectively prior to entering the field. Sample collection gear and samples were handled only by personnel wearing non-contaminating polyethylene gloves. All sample collection equipment (excluding the sediment grab) was cleaned by using the following sequential process:

Two-day soak and wash in Micro® detergent, three tap-water rinses, three deionized water rinses, a three-day soak in 10% HCl, three ASTM Type II Milli-Q® water rinses, air dry, three petroleum ether rinses, and air dry.

All cleaning after the Micro® detergent step was performed in a positive pressure "clean" room to prevent airborne contaminants from contacting sample collection equipment. Air supplied to the clean room was filtered.

The sediment grab was cleaned prior to entering the field, and between sampling stations, by utilizing the following sequential steps: a vigorous Micro® detergent wash and scrub followed

by a sea-water rinse. The sediment grab was scrubbed with seawater between successive deployments at the same station to remove adhering sediments from contact surfaces possibly originating below the sampled layer.

Sample storage containers were cleaned in accordance with the type of analysis to be performed upon its contents. All containers were cleaned in a positive pressure "clean" room with filtered air to prevent airborne contaminants from contacting sample storage containers.

Plastic containers (HDPE or TFE) for trace metal analysis media (sediment, archive sediment, pore water, and subsurface water) were cleaned by: a two-day Micro® detergent soak, three tap-water rinses, three deionized water rinses, a three-day soak in 10% HCl or HNO₃, three Type II Milli-Q® water rinses, and air dry.

Glass containers for total organic carbon, grain size or synthetic organic analysis media (sediment, archive sediment, pore water, and subsurface water) and additional teflon sheeting cap-liners were cleaned by: a two-day Micro® detergent soak, three tap-water rinses, three deionized water rinses, a three-day soak in 10% HCl or HNO₃, three Type II Milli-Q® water rinses, air dry, three petroleum ether rinses, and air dry.

Sample Collection

All sampling locations (latitude & longitude), whether altered in the field or predetermined, were verified using a Garmin Global Positioning System, and recorded in the field logbook. The primary method of sediment collection was with a 0.1m² Young-modified Van Veen grab aboard a sampling vessel. Modifications include a non-contaminating Tefzel® coating which covered the grab's sample box and jaws. After the filled grab sampler was secured on the boat gunnel, the sediment sample was inspected carefully. The following acceptability criteria were met prior to taking sediment samples. If a sample did not meet all the criteria, it was rejected and another sample was collected.

1. Grab sampler was not over-filled (i.e., the sediment surface was not pressed against the top of the grab).
2. Overlying water was present, indicating minimal leakage.
3. Overlying water was not excessively turbid, indicating minimal sample disturbance.
4. Sediment surface was relatively flat, indicating minimal sample disturbance.
5. Sediment sample was not washed out due to an obstruction in the sampler jaws.
6. Desired penetration depth was achieved (i.e., 10 cm).
7. Sample was muddy (>30% fines), not sandy or gravelly.
8. Sample did not include excessive shell, organic or man-made debris.

It was critical that sample contamination be avoided during sample collection. All sampling equipment (i.e., siphon hoses, scoops, containers) was made of non-contaminating material and was cleaned appropriately before use. Samples were not touched with un-gloved fingers. In addition, potential airborne contamination (e.g., from engine exhaust, cigarette smoke) was avoided. Before sub-samples from the grab sampler were taken, the overlying water was removed by slightly opening the sampler, being careful to minimize disturbance or loss of fine-grained surficial sediment. Once overlying water was removed, the top 5 cm of surficial

sediment was sub-sampled from the grab. Subsamples were taken using a precleaned flat bottom HDPE scoop. This device allowed a relatively large sub-sample to be taken from a consistent depth. When subsampling surficial sediments, unrepresentative material (e.g., large stones or vegetative material) was removed from the sample in the field. Small rocks and other small foreign material remained in the sample. Determination of overall sample quality was determined by the chief scientist in the field. Such removals were noted on the field data sheet. For the sediment sample, the top 5 cm was removed from the grab and placed in a pre-labeled polycarbonate container. Between subsequent grabs, the container was covered with a lid and kept cool. When a sufficient amount of sediment was collected, the sample was sealed and placed on wet ice for transport to the laboratory.

Benthic infaunal samples (n=12) were opportunistically collected at a subset of sampling locations. Sediment cores were sieved through a 0.5 mm screen and residues (e.g., organisms and remaining sediments) were rinsed into containers and preserved with a 10% formaldehyde solution. After 3 to 4 days, samples were rinsed and transferred into 70% isopropyl alcohol. These samples were archived for possible sorting and taxonomic identification at a later date.

Discrete Water Measurements/Water Quality Profiles

Water quality was measured at three depths (surface, mid-depth, near bottom) using a Hydrolab DataSonde. Temperature, pH, oxygen concentration (dissolved oxygen and oxygen saturation), depth and salinity were recorded at each depth. In addition, discrete water samples were collected at the same depths using a 1-liter Kemmerer water sampler for turbidity analysis in the field using a LaMotte2020 Turbidimeter.

Transport of Samples

Six-liter sample containers were packed (three to an ice chest) with enough ice to keep them cool for 48 hours. Each container was sealed in precleaned, large plastic bags closed with a cable tie to prevent contact with other samples or ice or water. Ice chests were transported back to the laboratory following the sampling cruise.

Homogenization and Aliquoting of Samples

Samples remained in ice chests (on ice, in double-wrapped plastic bags) until the containers were brought back to the laboratory for homogenization. All sample identification information (station numbers, etc.) was recorded on Chain of Custody (COC) and Chain of Record (COR) forms prior to homogenizing and aliquoting. A single container was placed on plastic sheeting while also remaining in original plastic bags. The sample was stirred with a polycarbonate rod until mud appeared homogeneous.

All prelabeled jars were filled using a clean teflon or polycarbonate scoop and stored in freezer/refrigerator (according to media/analysis) until analysis. The sediment sample was aliquoted into appropriate containers for grain size, TOC, trace metal analysis, and organic analysis. Samples were placed in boxes sorted by analysis type. Sample containers for sediment chemistry (metals, organics) were stored in a freezer (-20°C) until distributed to the appropriate analytical laboratory.

Chain of Records & Custody

Chain-of-records documents were maintained for each station. Each form was a record of all sub-samples taken from each sample. Station numbers and station names, date and time collected were included on each sheet. A Chain-of-Custody form accompanied every sample so that each person releasing or receiving a subsample signed and dated the form.

Trace Metals Analysis of Sediments

Summary of Methods

Trace metal analyses were conducted at the California Department of Fish and Game's (CDFG) Marine Pollution Studies Laboratory at Moss Landing, CA. Table 1 indicates the trace metals analyzed and lists method detection limits for sediments. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to determine trace metal concentrations in sediments. A full description of the performance based methods and procedures can be found in the U.S. EPA publication Method 200.7, Trace Elements in Water, Solids, and Biosolids by Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 5.0, August 1998 (USEPA 1998).

Analytes and Detection Limits

Table 2. Trace reporting limits in sediments ($\mu\text{g/g}$, dry weight)

Element	Reporting Limit ($\mu\text{g/g}$, dry weight)
Arsenic	0.1
Cadmium	0.002
Chromium	0.03
Copper	0.003
Lead	0.002
Silver	0.008
Zinc	0.02

Sediment Digestion Procedures

One half gram aliquot of sediment was placed in a pre-weighed Teflon vessel, and 5 ml of concentrated double distilled nitric acid and 3 ml of hydrofluoric acid mixture was added. The vessel was capped and digested in a CEM Microwave Accelerate Reaction System 5 using the following steps: 15 minute ramp to 195°C and 250psi (controlled by temperature), 20 minute hold at temperature and pressure, 20 minute cool down cycle. Once cool, 20 ml of 2.5% Boric Acid are added to each vessel. The samples are returned to the microwave to undergo the following: 5 minute ramp to 195°C and 250psi (controlled by temperature), 15 minute hold at temperature and pressure, 20 minute cool down. The vessels are allowed to cool completely and vented. Then the final weight is recorded before the digestates are transferred into pre-cleaned polyethylene bottles.

ICP_AES Methods

Samples were analyzed by ICP-AES on a Perkin-Elmer Elan 6000 ICPMS. Samples, blanks, and standards were prepared using clean techniques inside a clean laboratory. ASTM Type II

water and ultra clean chemicals were used for all standard preparations. Continuing calibration check standards (CLC) were analyzed with each sample batch, and a calibration standard was run after every 10 samples. Blanks and standard reference materials, MESS1 or PACS were analyzed with each set of samples for sediments.

Trace Organic Analysis of Sediments (Polycyclic Aromatic Hydrocarbons (PAHs))

Table 3: Subset of PAHs analyzed and their reporting limits in sediment (ng/g dry weight)

PAH	Reporting Limit (ng/g dry weight)
Naphthalene	5
2-Methylnaphthalene	5
1-Methylnaphthalene	5
Biphenyl	5
2,6-Dimethylnaphthalene	5
Acenaphthylene	5
Acenaphthene	5
2,3,5-Trimethylnaphthalene	5
Fluorene	5
Phenanthrene	5
Anthracene	5
1-Methylphenanthrene	5
Fluoranthrene	5
Pyrene	5
Benz[a]anthracene	5
Chrysene	5
Benzo[b]fluoranthrene	5
Benzo[k]fluoranthrene	5
Benzo[e]pyrene	5
Benzo[a]pyrene	5
Perylene	5
Indo[1,2,3-cd]pyrene	5
Dibenz[a,h]anthracene	5
Benzo[ghi]perylene	5

Extraction and Analysis

Sets of 12-16 homogenized sediment samples are scheduled for extraction by the project lead chemist. Extraction methods employed were developed and validated by the Water Pollution Control Laboratory. Extract cleanup and partitioning methods are modifications of the multi-residue methods for solids described in EPA Method 3500B-3545 from EPA Test Methods for Evaluating Solid Waste Vol. 1B.

Homogenized sediment samples are removed from the freezer and allowed to thaw. A separate extraction bench sheet is initiated for each project, sample matrix type, and analysis type.

A 1-5 g (sediment homogenate) sample is weighed into a pre-weighed aluminum planchet and placed in a 70°C oven for 48 hours to determine moisture content. A 10 g sample is mixed using a clean glass stirring rod with approximately 7 g of pre-extracted (twice) Hydromatrix (Varian Part NO: 0019-8003) in a 250 mL Trace Clean Wide Mouth Jar until the mixture is free flowing. The mixture is then poured into a 33 ml stainless steel Dionex Accelerated Solvent Extractor (ASE 200) extractor cell and packed by tamping the mixture. A solution containing PAH surrogate compounds is added to the cell and the cap is screwed onto the cell. The extractor cells (maximum of 24) are placed on the ASE 200 autosampler rack and the samples are extracted twice with a 50/50 mixture of acetone/dichloromethane (DCM) using heat and pressure. The extracts are automatically collected in 60 ml VOA vials. The extracts are combined and dried using sodium sulfate, evaporated to approximately 0.5 ml using Kuderna-Danish (K-D) glassware equipped with 3-ball Snyder columns and micro-Snyder apparatus and diluted to 10 mL using DCM. The extracts are then filtered through a 0.45 µm syringe filter into J2 Scientific AccuPrep 170 (GPC) autosampler tubes equipped with teflon septum lined caps.

The GPC autosampler tubes are then placed on the GPC autosampler for initial sample cleanup. All samples are cleaned up using the large GPC column. The cleaned-up extracts are evaporated using K-D apparatus and solvent exchanged into pentane. The extracts are then fractionated using a standard 10 mm x 300 mm small column packed with 1 ml sodium sulfate (drying agent), 2 ml alumina, 4 ml silica and another 1 ml sodium sulfate. The alumina/silica columns are eluted with 1:1 dichloromethane:pentane. The fractions are concentrated to an appropriate volume using K-D/micro K-D apparatus prior to analysis by gas chromatography/mass spectroscopy.

The extract was divided into two portions, one for chlorinated hydrocarbon (CH) analysis and the other for polycyclic aromatic hydrocarbon (PAH) analysis. The CH portion was eluted through a silica/alumina column, separating the analytes into two fractions. Fraction 1 (F1) was eluted with 1% methylene chloride in pentane and contains > 90% of p,p'-DDE and < 10% of p,p'-DDT. Fraction 2 (F2) analytes were eluted with 100% methylene chloride. The two fractions were exchanged into hexane and concentrated to 500 l using a combination of rotary evaporation, controlled boiling on tube heaters, and dry nitrogen blow downs. F1 and F2 fractions were analyzed on Hewlett-Packard 5890 Series gas chromatographs utilizing capillary columns and electron capture detection (GC/ECD). A single 2 l splitless injection was directed onto two 60m x 0.25mm i.d. columns of different polarity (DB-17 & DB-5; J&W Scientific) using a glass Y-splitter to provide a two dimensional confirmation of each analyte. Analytes were quantified using internal standard methodologies. The extract s PAH portion was eluted through a silica/alumina column with methylene chloride. It then underwent additional cleanup using size-exclusion high performance liquid chromatography (HPLC/SEC). The collected PAH fraction was exchanged into hexane and concentrated to 250 l in the same manner as the CH fractions.

Total Organic Carbon Analysis of Sediments

Summary of Methods

Samples were received in the frozen state and allowed to thaw at room temperature. Source samples were gently stirred and sub-samples were removed with a stainless steel spatula and placed in labeled 20 ml polyethylene scintillation vials. Approximately 5 grams equivalent dry weight of the wet sample was sub-sampled.

Sub-samples were treated with two, 5 ml additions of 0.5 N, reagent grade HCl to remove inorganic carbon (CO_3^{2-}), agitated, and centrifuged to a clear supernate. Some samples were retreated with HCl to remove residual inorganic carbon. The evolution of gas during HCl treatment indicates the direct presence of inorganic carbon (CO_3^{2-}). After HCl treatment and decanting, samples were washed with approximately 15 ml of deionized-distilled water, agitated, centrifuged to a clear supernate, and decanted. Two sample washings were required to remove weight determination and analysis interferences.

Prepared samples were placed in a 60 °C convection oven and allowed to come to complete dryness (approximately 48 hrs). Visual inspection of the dried sample before homogenization was used to ensure complete removal of carbonate containing materials (e.g., shell fragments). Two 61 mm (1/4") stainless steel solid balls were added to the dried sample, capped and agitated in a commercially available ball mill for three minutes to homogenize the dried sample.

A modification of the high temperature combustion method, utilizing a Wheatstone bridge current differential was used in a commercially available instrument (Control Equipment Co., 440 Elemental Analyzer) to determine carbon and nitrogen concentrations. The manufacturers suggested procedures were followed. The methods are comparable to the validation study of USEPA method MARPCPN I. Two to three aliquotes of 5-10 mg of dried prepared sub-sample were used to determine carbon and nitrogen weight percent values. Calibration of the instrument was with known standards using Acetanilide or L-Cystine. Detection limits are 0.2 ug/mg, carbon and 0.01 ug/mg nitrogen dry weight.

The above methods and protocols are modifications of several published papers, reference procedures, and analytical experimentation experience (Franson, 1981; Froelich, 1980; Hedges and Stern, 1983; MARPCPN I, 1992).

Quality control was tested by the analysis of National Research Council of Canada Marine Sediment Reference Material, BCSS-1 at the beginning and end of each sample analysis set (20-30 individual machine analyses). All analyzed values were within suggested criteria of $\pm 0.09\%$ carbon (2.19% Average). Nitrogen was not reported on the standard data report, but was accepted at $\pm 0.008\%$ nitrogen (0.195% Average) from the EPA study. Quality assurance was monitored by re-calibration of the instrument every twenty samples and by the analysis of a standard as a unknown and comparing known theoretical percentages with resultant analyzed percentages. Acceptable limits of standard unknowns were less than $\pm 2\%$. Duplicate or triplicate sample analysis variance (standard deviation/mean) greater than 7% is not accepted. Samples were re-homogenized and re-analyzed until the variance between individual runs fell below the acceptable limit of 7.0%.

Grain Size Analysis of Sediments

Summary of Methods

The procedure used combined wet and dry sieve techniques to determine particle size of sediment samples. Methods follow those of Folk (1974).

Sample Splitting and Preparation

Samples were thawed and thoroughly homogenized by stirring with a spatula. Spatulas were rinsed of all adhering sediment between samples. Size of the subsample for analysis was determined by the sand/silt ratio of the sample. During splitting, the sand/silt ratio was estimated and an appropriate sample weight was calculated. Subsamples were placed in clean, pre-weighed beakers. Debris was removed and any adhering sediment was washed into the beaker.

Wet Sieve Analysis (separation of coarse and fine fraction)

Beakers were placed in a drying oven and sediments were dried at less than 55 °C until completely dry (approximately three days). Beakers were removed from the drying oven and allowed to equilibrate to room temperature for a least a half-hour. Each beaker and its contents were weighed to the nearest 0.01 g. This weight minus the empty beaker weight was the total sample weight. Sediments in beakers were disaggregated using 100 ml of a dispersant solution in water (such as 50g Calgon/l water) and the sample was stirred until completely mixed and all lumps disappear. The amount and concentration of dispersant used was recorded on the data sheet for each sample. Sample beakers were placed in an ultrasonic cleaner for 15 minutes for disaggregation. Sediment dispersant slurry was poured into a 63 µm (ASTM #230, 4 phi) stainless steel or brass sieve in a large glass funnel suspended over a 1 l hydrometer cylinder by a ring stand. All fine sediments were washed through the sieve with water. Fine sediments were captured in a 1l hydrometer cylinder. Coarse sediments remaining in sieve were collected and returned to the original sample beaker for quantification.

Dry Sieve Analysis (coarse fraction)

The coarse fraction was placed into a pre-weighed beaker, dried at 55-65 °C, allowed to acclimate, and then weighed to 0.01 g. This weight, minus the empty beaker weight, was the coarse fraction weight. The coarse fraction was poured into the top sieve of a stack of ASTM sieves having the following sizes: No. 10 (2.0 mm), 18 (1.0 mm), 45 (0.354 mm), 60 (0.25 mm), 80 (0.177 mm), 120 (0.125 mm), and 170 (0.088 mm). The stack was placed on a mechanical shaker and shaken at medium intensity for 15 minutes. After shaking, each sieve was inverted onto a large piece of paper and tapped 5 times to free stuck particles. The sieve fractions were added cumulatively to a weighing dish, and the cumulative weight after each addition determined to 0.01g. The sample was returned to its original beaker, and saved until sample computations were completed and checked for errors.

Analytical Procedures

Fractional weights and percentages for various particle size fractions were calculated. If only wet sieve analysis was used, weight of fine fraction was computed by subtracting coarse fraction from total sample weight, and percent fine composition was calculated using fine fraction and total sample weights. If dry sieve was employed as well, fractional weights and percentages for the sieve were calculated using custom software on a Macintosh computer. Calibration factors were stored in the computer.

Quality Assurance/Quality Control

Summary of Methods

Detailed descriptions of quality assurance and quality control procedures are described under separate cover in the Surface Waters Ambient Monitoring Program (SWAMP) Quality Assurance Project Plan (QAPP). This document describes procedures within the program that

ensure data quality and integrity and can be viewed or downloaded from the SWAMP website at <http://www.swrcb.ca.gov/swamp/qapp.html>. Quality assurance procedures for this project were followed in accordance to SWAMP guidelines. In addition, individual laboratories prepare quality assurance evaluations of each discrete set of samples analyzed and authorized by task order. These documents were submitted to MLML-MPSL for further review.

Chemical Specific Sediment Quality Guidelines

There have been several recent studies associating pollutant concentrations with biological responses (Long and Morgan, 1990; MacDonald, 1992). These studies provide guidance for evaluating the degree to which chemical pollutants from field collected sediments are associated with effects observed in toxicity tests. Reported guidance values are based on individual chemical pollutants within sediments so their application may be confounded when dealing with biological effects which could be attributed to a synergistic effect of low levels of multiple chemicals, unrecognized chemicals, or physical parameters in the sediment that were not measured. They do however provide empirical sediment quality guidelines (SQGs) that can be used as screening tools to help predict when chemical conditions have an increased probability of toxicity and/or biological community impairment. In this study the chemical results for individual trace metals and PAHs (also PAH groupings) were compared to their respective SQGs.

The National Status and Trends Program has used chemical and toxicological evidence from a number of modeling, field and laboratory studies to determine the ranges of chemical concentrations which are rarely, sometimes, or usually associated with toxicity (Long and Morgan, 1992). Evaluation of available data (Long *et al.*, 1995) has led to identification of three ranges in concentration for each chemical:

- 1) Minimal Effects Range: The range in concentration over which toxic effects are rarely observed;
- 2) Possible Effects Range: The range in concentrations over which toxic effects are occasionally observed;
- 3) Probable-Effects Range: The range in chemical concentrations over which toxic effects are frequently, or always, observed.

Two slightly different methods were used to determine these chemical ranges. One method developed by NOAA (Long and Morgan, 1990; Long *et al.*, 1995) used chemical data that were associated with a toxic biological effect. These data were used to determine the lower 10th percentile of ranked data where the chemical level was associated with an effect (Effects Range-Low, or ERL). Sediment samples in which all chemical concentrations were below the 25 ERL values were not expected to be toxic. The Effects Range-Median (ERM) reflects the 50th percentile of ranked data and represents the level above which effects are expected to occur. Effects are expected to occur occasionally when chemical concentrations fall between the ERL and ERM (Table 3). The probability of toxicity was expected to increase with the number and degree of exceedances of the ERM values.

Another method identifies three ranges using chemical concentration data associated with both toxic biological effects and no observed effects (MacDonald, 1992; MacDonald, 1994;

MacDonald *et al.*, 1996). The ranges are identified as TEL (Threshold Effects Level) and the PEL (Probable Effects Level). TEL values were derived by taking the geometric mean of the 50th percentile of the "no effects" data and the 15th percentile of the "effects" data. The PEL values were derived by taking the geometric mean of the 85th percentile of the "no effects" data and the 50th percentile of the "effects" data. Although different percentiles were used for these two methods, they are in close agreement, usually within a factor of 2. Values reported for both methods are shown in Table SQG. Neither of these methods is advocated over the use of the other in this report. Instead, both are used in the following analysis to create a weight of evidence that should help explain the relationships between observed chemical concentrations and the probability that a biological effect would be associated with that particular sediment chemical.

Because this study focused on polycyclic aromatic hydrocarbons (PAHs), an additional sediment quality guideline that focuses specifically on PAH mixtures was considered. PAHs virtually always occur in field collected sediments as a complex mixture of covarying compounds so Swartz (1999) proposed a consensus based guideline value based on a mixture of 13 PAH compounds that the USEPA identified as priority pollutants. This consensus guideline value (Table 3) is particularly useful because it allows estimates of ecological risk due to the cumulative effects of multiple PAHs. It also relies on a normalization approach with organic carbon that helps address the bioavailability of PAHs in organic rich sediments where binding of organic chemicals is enhanced.

In addition to these national guidelines, there has been an extensive regional effort at determining ambient chemical concentrations in the sediments of San Francisco Bay. Regional Board Resolution 92-145 was published to establish screening criteria for the beneficial reuse of dredged sediments in San Francisco Bay (SWRCB, 1992). As part of that effort and the work of other organizations, the basis of ambient chemical concentrations in San Francisco Bay was developed (SWRCB, 1998). Although the ambient concentrations (Table 3) are not meant to be used as screening values, by comparing sediment chemical concentrations within the marinas to ambient conditions, it is possible to gain the context for predicting whether marina sediments fall within the range of what is expected as ambient or whether they are potentially elevated. In this report, comparisons are made to both sediment quality guidelines and to ambient concentrations for as many chemicals as possible.

For comparative purposes, two other sets of sediment quality guidelines are presented in Table 4. The first was established for the State of Washington and are called Apparent Effect Thresholds (AET; PTI, 1991). AET values are concentration above which biological effects are always expected to occur. The second set were sediment criteria developed by the USEPA (1993) using an equilibrium partitioning (EqP) approach for several individual PAHs.

Table 4. Sediment quality guidelines and San Francisco Bay ambient chemical concentrations

Chemical Name	ERL	ERM	TEL	PEL	Other SQGs	Ambient
Arsenic	8.2 ug/g	70 ug/g	7.24 ug/g	41.6 ug/g	700 ug/g [1]	15.3 ug/g
Cadmium	1.2 ug/g	9.6 ug/g	0.68 ug/g	4.21 ug/g	n/a	0.33 ug/g
Chromium	81 ug/g	370 ug/g	52.3 ug/g	160.4 ug/g	270 ug/g [1}	112 ug/g

Copper	34 ug/g	270 ug/g	18.7 ug/g	108.2 ug/g	1300 ug/g [1]	68.1 ug/g
Lead	46.7 ug/g	218 ug/g	30.2 ug/g	112.18 ug/g	660 ug/g [1]	43.2 ug/g
Nickel	20.9 ug/g	51.6 ug/g	15.9 ug/g	42.8 ug/g	n/a	112 ug/g
Mercury	0.15 ug/g	0.71 ug/g	0.13 ug/g	0.7 ug/g	n/a	0.43 ug/g
Silver	1.0 ug/g	3.7 ug/g	0.73 ug/g	1.77 ug/g	6.1 ug/g [1]	0.58 ug/g
Zinc	150 ug/g	410 ug/g	124 ug/g	271 ug/g	1600 ug/g [1]	158 ug/g
Acenaphthene	16 ng/g	500 ng/g	6.71 ng/g	88.9 ng/g	230 ug/g OC [2]	26 ng/g
Acenaphthylene	44 ng/g	640 ng/g	5.87 ng/g	127.89 ng/g	n/a	88 ng/g
Anthracene	85.3 ng/g	1100 ng/g	46.9 ng/g	245 ng/g	n/a	88 ng/g
Fluorene	19 ng/g	540 ng/g	21.2 ng/g	144.35 ng/g	n/a	19 ng/g
2-methylnapthalene	70 ng/g	670 ng/g	20.2 ng/g	201.28 ng/g	n/a	19.4 ng/g
Napthalene	160 ng/g	2100 ng/g	34.6 ng/g	390.64 ng/g	n/a	55.8 ng/g
Phenanthrene	240 ng/g	1500 ng/g	86.7 ng/g	543.53 ng/g	240 ug/g OC [2]	237 ng/g
Low m.w. PAHs	552 ng/g	3160 ng/g	312 ng/g	1442 ng/g	24000 ng/g [1]	434 ng/g
Benz[a]anthracene	261 ng/g	1600 ng/g	74.8 ng/g	692.53 ng/g	n/a	412 ng/g
Benzo[a]pyrene	430 ng/g	1600 ng/g	88.8 ng/g	763.22 ng/g	n/a	371 ng/g
Chrysene	384 ng/g	2800 ng/g	108 ng/g	845.98 ng/g	n/a	289 ng/g
Dibenz[a,h]anthracene	63.4 ng/g	260 ng/g	6.22 ng/g	134.61 ng/g	n/a	32.7 ng/g
Fluoranthene	600 ng/g	5100 ng/g	113 ng/g	1493.54 ng/g	300 ug/g OC [2]	514 ng/g
Pyrene	665 ng/g	2600 ng/g	153 ng/g	1397.6 ng/g	n/a	665 ng/g
High m.w. PAHs	1700 ng/g	9600 ng/g	655 ng/g	6676.14 ng/g	69000 ng/g [1]	3060 ng/g
Total PAHs	4022 ng/g	44792 ng/g	1684 ng/g	16770.54 ng/g	1800 ug/g OC [3]	3390 ng/g

ERL and ERM values were taken from Long *et al.*, 1995; TEL and PEL values were taken from MacDonald *et al.*, 1996

Other SQGs were taken from [1] PTI Environmental Services (AETs); [2] USEPA, 1993 (EqP) and [3] Swartz, 1999 (Consensus); Ambient values were taken from SWRCB, 1998

Statistical Analyses

A One Way Analysis of Variance (ANOVA) was used to determine if there was a difference in analyte concentration among harbors. If a particular analyte met the assumptions of an ANOVA (e.g., normality), a parametric One Way ANOVA was run grouped by marinas (four marinas and Paradise Cove). If there was a significant difference due to the marinas, then each pairwise comparison was tested with a Tukey test to determine where significant differences existed among the marinas. The Tukey test was chosen because it is a conservative test and a Type I error (i.e., reject a true null hypothesis) would less likely occur. If the data was not normally distributed, a non-parametric Kruskal-Wallis One Way ANOVA, which is based on ranks, was run. Pairwise comparisons were made with the Dunn's method without adjustment for ties.

To determine the strength of association between various analytes (e.g., between arsenic and cadmium), a Pearson Product Moment Correlation was used. The correlation coefficient (r) ranges between -1 and 1 in which a value near 1 indicates a positive relationship with both variables increasing together. A value near -1 suggests a negative relationship with one variable always increasing as the other decreases. A value near 0 indicates no association. All statistical analyses were performed with SigmaStat and a p value less than or equal to 0.05 was used to determine a significant difference.

RESULTS AND DISCUSSION

Data Management and Quality

Tabulated data for all field information and chemical analyses are stored in a MS Access database. The database structure used for reporting the current data is the same used by the SWAMP program for reporting environmental monitoring data. This format was selected so that the marina survey data could be uploaded to the SWAMP database and shared via the web to future data users. The SWAMP Information Management (IM) plan describes the business rules for data capture and storage, the organizational table structures, data formats and data flow for the SWAMP program. The IM plan can be downloaded from <http://www.swrcb.ca.gov/swamp/qapp.html#appendixi> in Appendix J where updated versions are presented on the State Water Resources Control Board's SWAMP website. Data were exported from the SWAMP database in MS EXCEL and SYSTAT for manipulation and analysis. Data is to be made available in EXCEL format (SFMarina_2003.xls) but can be delivered in ACCESS format on request. The summary data presented in the following results sections were used to demonstrate significant findings from the analysis of the full data set in the database.

Analytical results were required to meet data quality objectives (DQOs) specified in the SWAMP QAPP. Review of the analytical quality assurance information demonstrated some minor exceedances of the DQO's for the trace metals cadmium and lead. The lab duplicate vessel broke during one of the digestion (2003Dig24), therefore duplicate information was not available for one of the batches. In addition, the matrix spike % recovery was slightly elevated for cadmium and lead that pushes these samples outside required SWAMP DQOs. We believe this was a data entry error where the final matrix solution weight on the original digestion data sheet was incorrectly entered, however, we are unable to verify this supposition. All other QA objectives for the trace metal analyses were met and duplicates at stations in Berkeley (Stations 5 and 8 were blind field duplicates) and Paradise Cove (Stations 1 and 3 were blind field duplicates) demonstrated acceptable precision. It is recommended that all trace metal data be considered acceptable and valid in spite of the above noted minor DQO exceedances for cadmium and lead.

Review of the data quality for the PAH analyses revealed minor exceedances of some SWAMP DQOs. The matrix spike % recovery was slightly low for naphthalene in one sample. The surrogate corrected values for the standard reference material (SRM) were systematically high for the higher molecular weight PAHs so those values are not surrogate corrected. The C1,C2,C2 substituted results are considered screening values because the concentrations were calculated from the other standards (e.g. they didn't have standards for "C1 naphthalenes" so 1-methyl naphthalene was used to calculate it). Post extraction holding times were exceeded by 10 days due to instrumentation problems but should have no effect on data quality. Each of the above QA flags in the data are considered minor and do not diminish the quality of the data. All other QA objectives for the PAHs were met and duplicates at stations in Berkeley (Stations 5 and 8 were blind field duplicates) and Paradise Cove (Stations 1 and 3 were blind field duplicates) demonstrated acceptable precision. It is recommended that the sediment PAH results be considered acceptable and valid in spite of the above noted minor DQO exceedances.

Conventional Water Quality Parameters

Water quality measures were collected at the time of sampling to give a general sense of the range of physical conditions observed in the different marinas during the two days of sampling. Because the water quality measures are highly dependent on the time of sampling due to tidal cycle, light conditions, wind conditions, time of year, etc., the measures reported here should only be viewed as a snapshot in time and not necessarily representative of average or extreme conditions in each of the marinas. The measures are however useful in assessing relative differences among harbors at the time of sampling.

Temperature ranged from 15.9⁰ C to 24.3⁰ C (Figure 3) with the lowest temperatures measured in Corinthian Yacht Club and greatest temperatures measured in Loch Lomond Marina. Temperatures were stratified, with colder waters near bottom, within the confined marinas when compared to the well-mixed open waters at the reference stations in Paradise Cove.

Dissolved oxygen concentrations ranged from 2.4 mg/L to 9.3 mg/L (Figure 4) and also exhibited a pattern of depth stratification with measured oxygen concentrations lowest in near bottom waters. Ballena Isle Marina exhibited the lowest oxygen concentrations and demonstrated a concentration gradient where oxygen values decreased, moving from the front to the back of the marina. Bottom waters near the back of the marina had oxygen concentrations less than 4 mg/l suggesting hypoxic conditions that could impact biological activity. Similarly, three stations in the southeastern quarter of Berkeley marina exhibited bottom waters with low oxygen concentrations.

Salinity values ranged from 28.82 ppt to 35.01 ppt (Figure 5). Salinity values were consistent with depth within Berkeley, Ballena Isle and Loch Lomond marinas, but varied with depth at Corinthian Yacht Club and Paradise Cove. A strong flood tide occurred the morning of sampling and salinity stratification most likely reflects a lens of less saline waters from San Pablo Bay on top of marine waters brought in by tidal flow. Corinthian Yacht Club demonstrated the highest average salinities and the lowest average temperatures at the time of sampling, indicating a strong tidal influence of offshore marine waters from flowing into the marina. This pattern is expected, except the very high salinity value of 35.01 in the back bottom waters of Corinthian Yacht Club, that coincidentally also had the lowest temperature values and the greatest turbidity values. It is unclear if this high salinity value was real or an instrumental artifact, though instrument calibrations were all within acceptable ranges.

Turbidity measures ranged from 3.02 NTU to 37.9 NTU (Figure 6). Turbidity measures were stratified at all marina stations where near bottom waters were consistently more turbid than mid-depth or surface waters. Bottom waters in the back areas of Corinthian Yacht Club demonstrated the greatest turbidity.

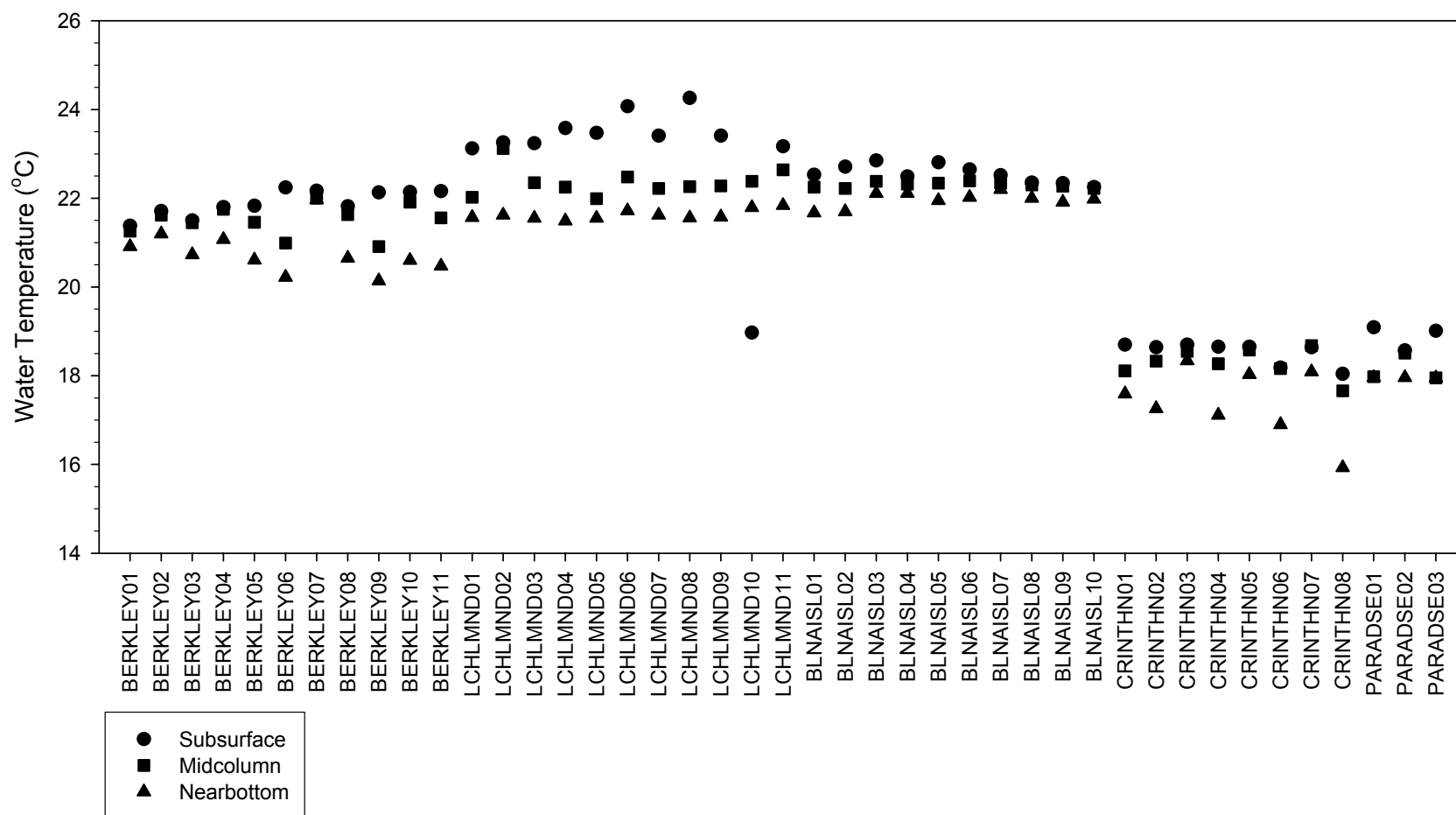


Figure 3. Histogram of water temperature in the marinas and reference site.

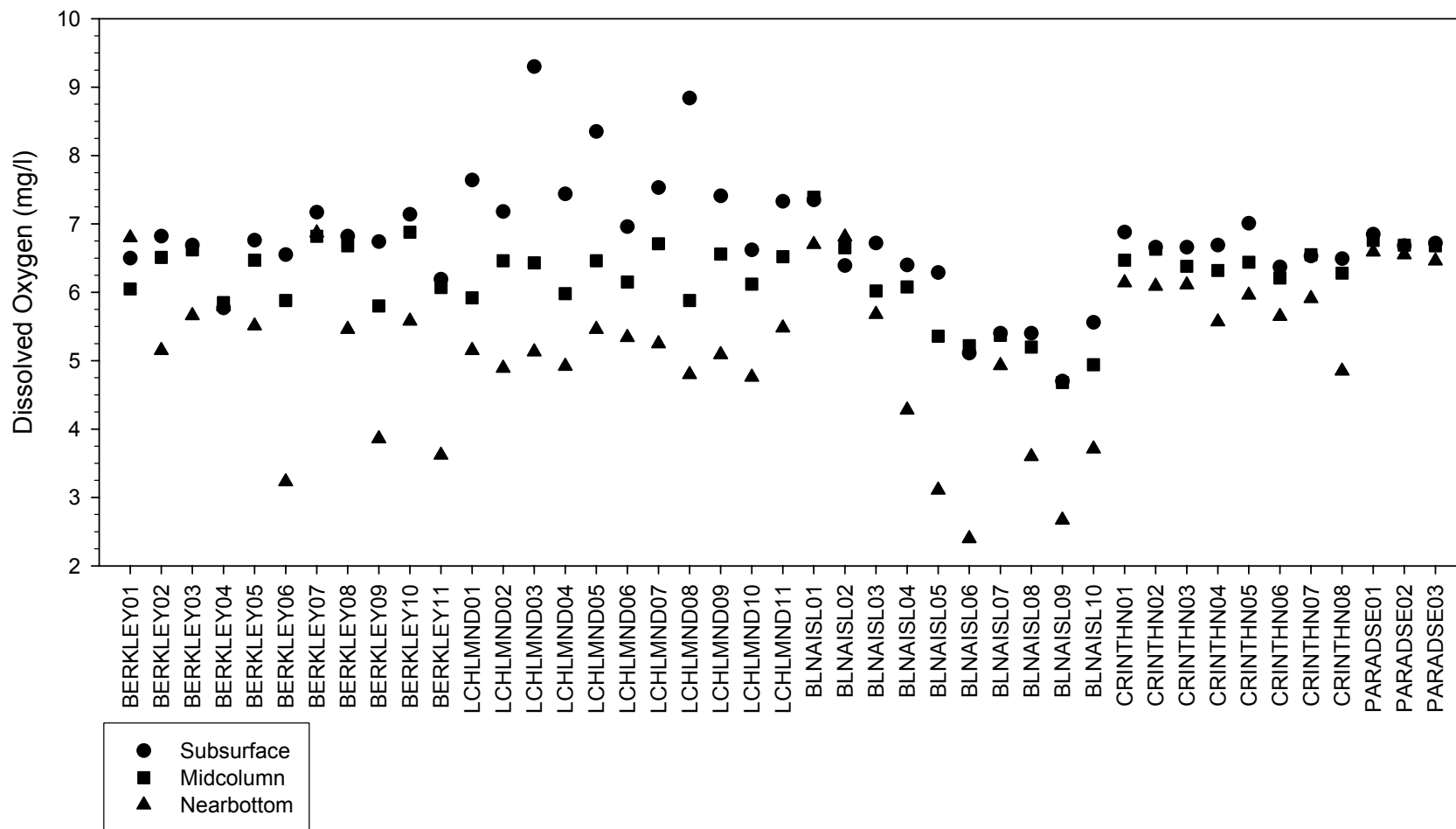


Figure 4. Histogram of dissolved oxygen in the marinas and reference site.

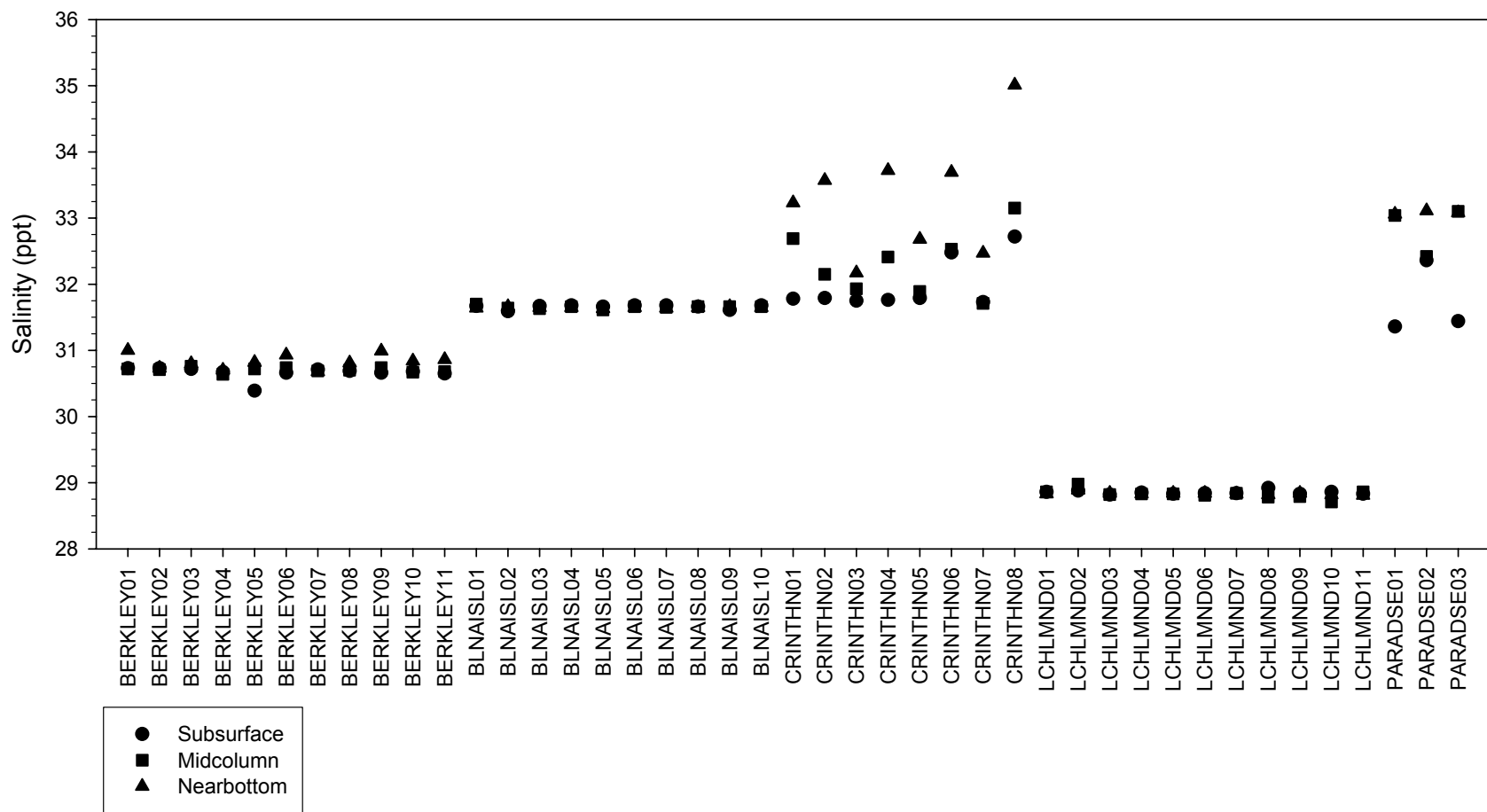


Figure 5. Histogram of salinity (ppt) in the marinas and reference site.

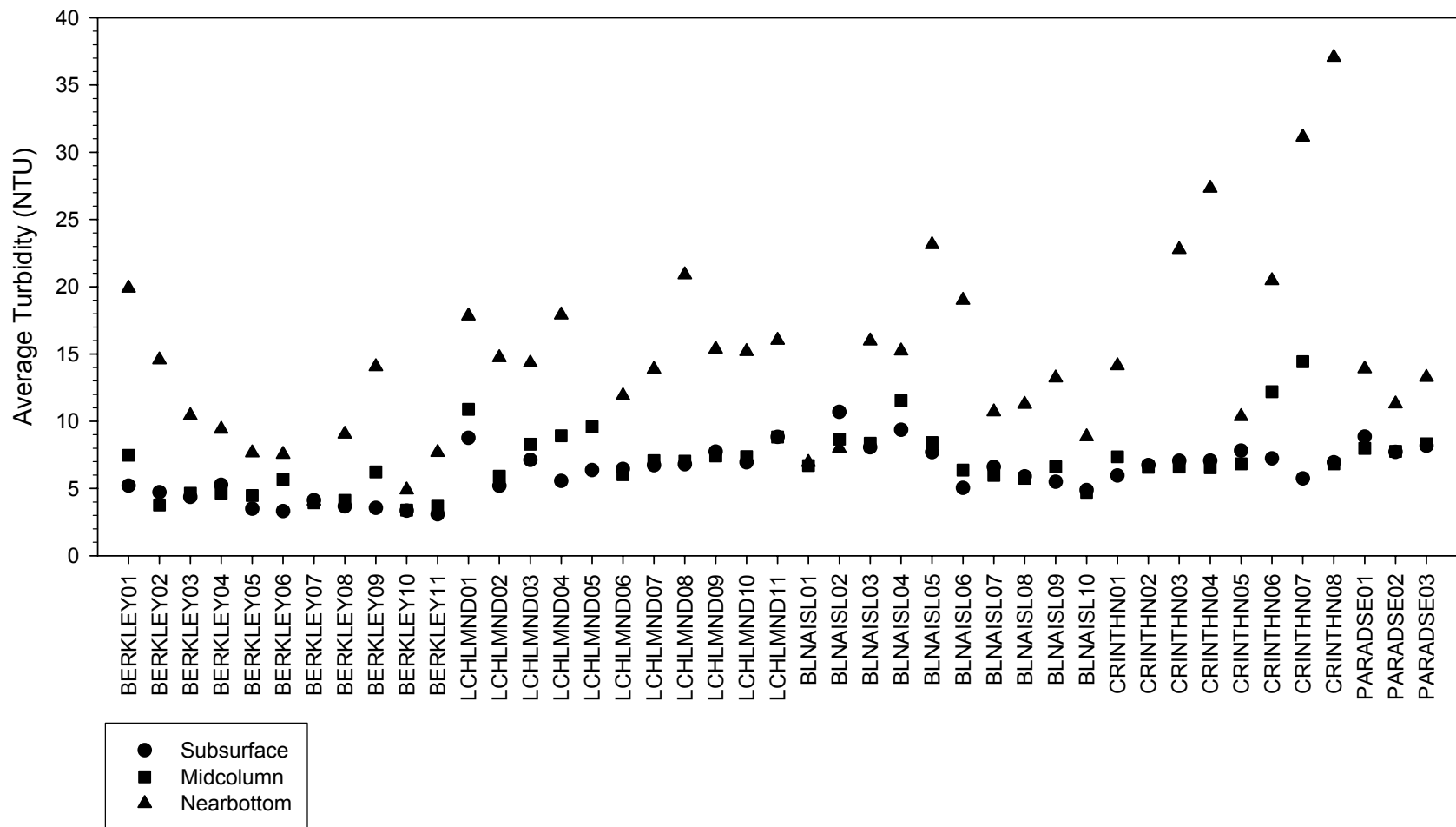


Figure 6. Histogram of average turbidity in the marinas and reference site.

Sediment Grain Size and Total Organic Carbon

Sediment grain size measures were taken to assess general physical characteristics of marina sediments and to compare relative differences in sediment characteristics among marinas. Sediment grain size measures ranged from 73.7% silt/clays to 99.9% silt/clays though most stations were well above 95% (Figure 7). The only obvious pattern was seen at Corinthian Marina where relatively more coarse grained sediments were found at the more exposed mouth of the marina and more fine sediments were found in the flow restricted back areas of the marina. Coarse grained sediments were measured at several locations in Berkeley and Loch Lomond marinas, but these locations had shell debris in the sample that were mixed with the silts and clays. Other than these shell debris locations, the marinas and reference site all had similar grain size characteristics, primarily fine mud dominated by silt and clay fractions. No obvious sediment type differences related to boating or dredging activities could be discerned.

Organic carbon is a major factor in controlling the bioavailability of nonionic organic compounds in sediments. This is based on equilibrium partitioning theory (EqP) in which the partitioning of organic chemicals is controlled by the equilibrium between sediment organic carbon and interstitial waters. Sediments that are organically rich tend to bind organic compounds and lower pore water concentrations thus reducing the major exposure route and subsequently bioavailability. To account for the freely dissolved concentration of organic chemicals in pore water, Total organic carbon (TOC) is often used to normalize compounds for comparison to published sediment quality guidelines (PTI, 1991; Swartz, 1999). TOC was measured at all locations in the current survey and concentrations ranged from 0.73% to 1.77% organic carbon. Ballena Isles Marina and Berkeley Marina demonstrated a concentration gradient where sediment TOC increased at stations moving from the front to the back of the marinas. TOC values are used later in this report to help predict the probability of toxicity from exposure to PAHs.

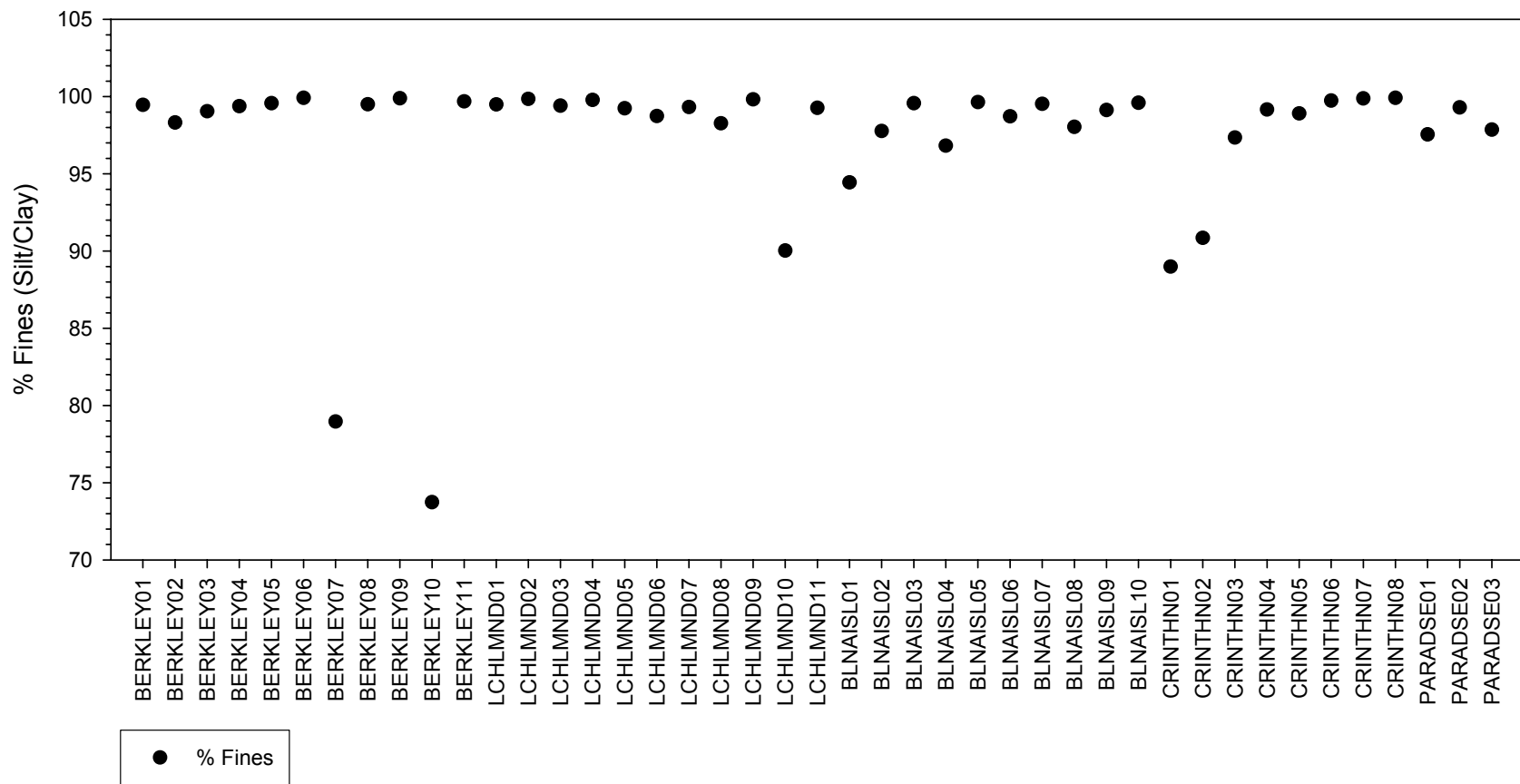


Figure 7. Histogram of grain size (% Fines) in the marinas and reference site

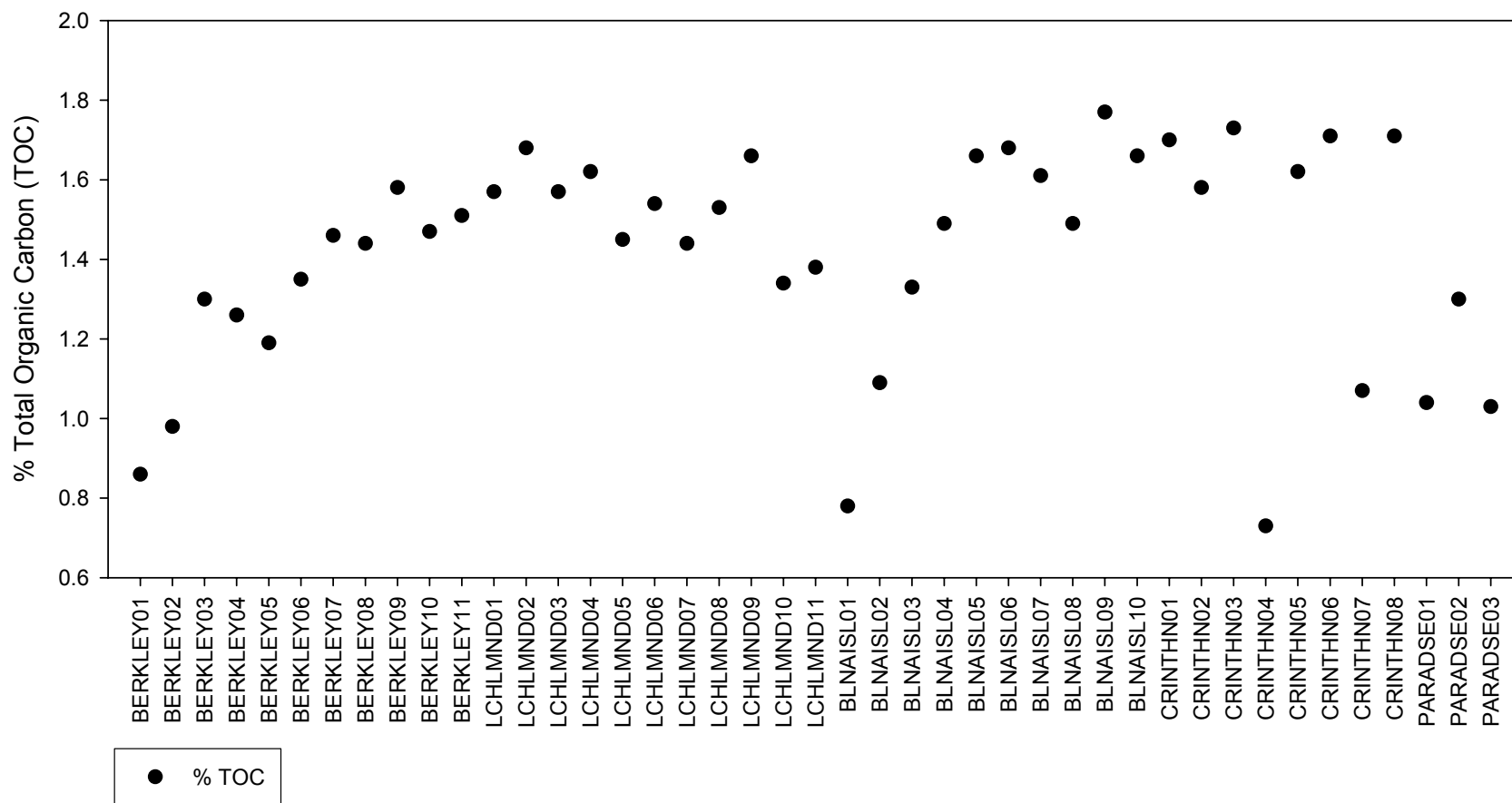


Figure 8. Histogram of total organic carbon (% TOC) in the marinas and reference site

Sediment Trace Metals and PAHs

Trace Metals

Arsenic. Arsenic, a metalloid, is often contained in paint pigments, wood treatments, and pesticides (U.S. EPA 2001). While marine paint and coating compounds made with arsenic are no longer used because of their toxicity, it is still used in CCA (chromated copper arsenate) treated wood in docks and pilings and may still be present on older boats. The toxicity of arsenic is highly dependent upon the nature of the arsenic compound (organic or inorganic) and the valence state of the arsenic atom. However, it is however total arsenic that is usually included in monitoring programs and is most often used as an indicator of arsenic contamination. Screening values for sediments are based on total arsenic so comparisons in this survey are made with total arsenic. Arsenic concentrations in the current survey ranged from 7.15 – 16.5 mg/kg (Figure 9), most of which exceeded the ERL of 8.2 mg/kg. Only one sample within Berkeley marina slightly exceeded Ambient concentrations for San Francisco Bay (16.5 vs 15.3 mg/kg), however the field duplicate sample was collected at the same location had measured arsenic concentrations slightly below Ambient. The relative percent difference between the duplicates (13%) is very reasonable considering field heterogeneity, so the one sample slightly above Ambient does not deserve undue attention. Considering the median/probable effects concentrations for arsenic (70 mg/kg - ERM and 41.6 mg/kg - PEL) are far from being exceeded, it is unlikely that any acute biological impacts would be associated with the observed arsenic concentrations. The study results indicate that total arsenic concentrations in the marinas are similar to ambient conditions throughout San Francisco Bay and currently present a low risk of toxicity in the marinas.

Copper. Copper is a broad spectrum biocide which may be associated with acute and chronic toxicity, reduction in growth, and a wide variety of sublethal effects (Spear and Pierce, 1979). Marina related sources of copper include anti-fouling paints and wood preservatives in docks and pilings. Copper (II) acetate is the common form used in fungicides, insecticides, mildew preventatives, corrosion inhibitors, fuel additives and anti-fouling paints. Sediment total copper concentrations in the current survey ranged from 38.2 – 151 mg/kg (Figure 10). Copper concentrations above the ERL (>34 mg/kg) were found at all locations throughout the San Francisco Bay marinas and approximately half the samples were elevated above Ambient concentrations for San Francisco Bay (68.1mg/kg; Figure 11). Four samples in Ballena Isle Marina and one in Berkeley were at or above the probable effects levels (108.2 mg/kg – PEL) though all samples were below ERM concentrations (270mg/kg – ERM). Values well above the ERL and expected Ambient values are notable because they represent an increased probability that adverse biological impacts could result from copper toxicity in the marinas. Copper should therefore be considered one of the major chemicals of concern in marinas. It should be noted however that the observed sediment copper concentrations are not indicative of high ecological risk. These represent a moderate probability of being associated with acute effects to aquatic life, and therefore worthy of management actions and future monitoring.

Pre-dredge testing of sediments in the front half of the marina (ABT, 1998) indicated copper concentrations that are very comparable to those measured in the current study. The current study sampled a larger area and found that copper concentrations are noticeably greater toward the back end of the marina. It is clear that a strong copper gradient exist in Ballena Isles Marina

but it is unclear if the lower copper concentrations toward the front of the marina are a result of recent dredging activities. It is plausible that maintenance dredging has removed accumulated sediment associated copper, while in place sediments toward the rear of the harbor reflect historical concentrations and/or more recent accumulations.

All marinas except Berkeley demonstrated a similar copper concentration gradient that increased geographically from the entrance to the inner areas of the marinas. Berkeley exhibited the same general trend however the fringes of the marina tended to have both low and high concentrations. The greatest concentration of copper observed in this study (151 mg/kg) was found near the boatyard and haul out area in the northwest corner of Berkeley marina. The Berkeley Marine Center, the marina's boatyard, tests the effluent of its water filtration system regularly and also samples storm water every fall, after the first rain. The source of copper within the sediments near the boatyard is still undetermined, however, untreated stormwater collected from the boatyard collection sump after November and December, 2003 rainfall events (Sequoia Analytical, 2003) demonstrated elevated concentrations of total copper (2100ug/l and 3400ug/l). This stormwater subsequently receives treatment for removal of contaminants and is not discharged into the marina, but it does point to the boatyard area as a potential copper source through stormwater runoff if activities are not carefully controlled. Although elevated copper in the marina sediments nearest the boatyard suggest a significant local source of copper loading to the marina, additional testing would be required to confirm and quantify this and other copper sources contributing to the sediment reservoir.

Cadmium. Cadmium compounds are used in the metal plating and battery industry, and as stabilizing agents in many polyvinyl chloride (PVC) products. Cadmium is a component of petrol, diesel fuel and lubricating oils. Cadmium is highly persistent in the environment and will concentrate or bioaccumulate in aquatic animals. Sediment total cadmium concentrations in the current survey ranged from 0.225 – 0.671 mg/kg (Figure 12). The greatest concentration of cadmium was observed in the back area of Ballena Isle marina (station 7) with a noticeable decreasing gradient at stations extending away from that area. The area around station 7 may be a source of cadmium to the rest of the marina and may warrant future investigation to better identify the extent of the contaminant and its likely source. In general, cadmium concentrations in the marinas were all near the expected San Francisco Bay Ambient concentrations and well below the ERL thresholds so have a low probability of posing a significant risk of acute effects to aquatic life.

Chromium. Chromium is chiefly found in its trivalent form in natural environments, except in seawater where chromium in its hexavalent state is prevailing, but at extremely low concentrations. Another oxidation state of practical importance is chromium (VI), but though there are some natural sources for chromium (VI), the majority originates from industrial activities. Compared to chromium (III), chromium (VI) is assumed to be about 100 to 1000 times more toxic. Chromium compounds are used for chrome plating (e.g. protective coatings for equipment accessories), as dyes, as inorganic paint pigments, and as fungicides and wood preservatives in docks and pilings. Chromium may be oxidized and leached from stainless steel into a water-soluble form. The U.S. EPA indicates that chromium has been used in various capacities in marinas and by boaters and can wash from parking lots, service roads, and launch ramps into surface waters with rainfall (U.S. EPA 2001). Sediment total chromium (III)

concentrations in the current survey ranged from 107 – 161 mg/kg (Figure 13). The greatest chromium concentration was observed in Ballena Isle Marina (BLNAIS08), interestingly very near the location where the greatest cadmium concentration was observed (BLNAIS07). It is possible that the cadmium and chromium sources in Ballena Isle Marina are in some way linked. Chromium concentrations increased along a gradient moving toward the back of the marinas in both Corinthian Yacht Club and Loch Lomond Marina. Chromium concentrations in the marinas and at the reference station were well all above the ERL and all but one were above San Francisco Bay Ambient concentrations. Chromium concentrations at several locations in Berkeley, Ballena Isle and Loch Lomond marinas approached or exceeded the probable effects level (PEL = 160.4mg/kg) and present an increased probability of biological impairment. Chromium should therefore be considered one of the major chemicals of concern in marinas and should be considered a moderate risk, worthy of management actions and future monitoring.

Lead. Marina and boating-related sources of lead compounds can include sailboat keels, marine paints, and lead acid batteries. Lead can be discharged into the marina environment from leaching of sailboat keels (Hinkey 2001), and corrosion of fittings and lead acid batteries (Washington State Department of Ecology 2001(a)). Lead is poisonous in all forms, is cumulative and the toxic effects are many and severe. Sediment total lead concentrations in the current survey ranged from 17.3 – 40.9 mg/kg (Figure 14). The greatest concentration (40.9 mg/kg) was observed near the boatyard in Berkeley Marina where other elevated metals have been observed. The next greatest lead concentration was observed in Ballena Isle Marina (BLNAIS08) at the same location where the greatest chromium concentration was observed. Lead concentrations in the marinas and at the reference station were all below the ERL thresholds and the San Francisco Bay Ambient concentrations, so appear to present a low probability of toxicity.

Zinc. Zinc anodes are commonly used as anti-corrodants for metal hulls, engine parts, and boat propeller shafts (U.S. EPA 2001). Zinc is also contained in boat anti-fouling paints (Hinkey 2001), motor oil, and tires, and is a common constituent of runoff from marina parking lots (U.S. EPA 2001), and zinc is a component of the wood preservative ACZA, which is used in marine pilings, docks and piers. Generally, zinc and its salts have high acute and chronic toxicity (particularly zinc chromate) to aquatic life and zinc chromate is listed as a potential carcinogen. Sediment total zinc concentrations in the current survey ranged from 82.7 – 219 mg/kg (Figure 15). The lowest mean values were measured in Corinthian Yacht Club and were in the same range as the reference station at Paradise Cove. The greatest mean values were measured in the back end of the Loch Lomond Marina. A zinc concentration gradient that increased geographically from the front to the back of the marinas was observed in both Ballena Isle and Loch Lomond marinas (Figure 16). The ERL and Ambient values for zinc are 150 and 158 mg/kg, respectively with about a third of the samples exhibiting concentrations above these guideline values. None of the samples exceeded ERM or PEL guidelines where acute effects would be more probable, however the large number of stations exceeding the lower guidelines may warrant some attention and future monitoring efforts to examine this pattern for any change.

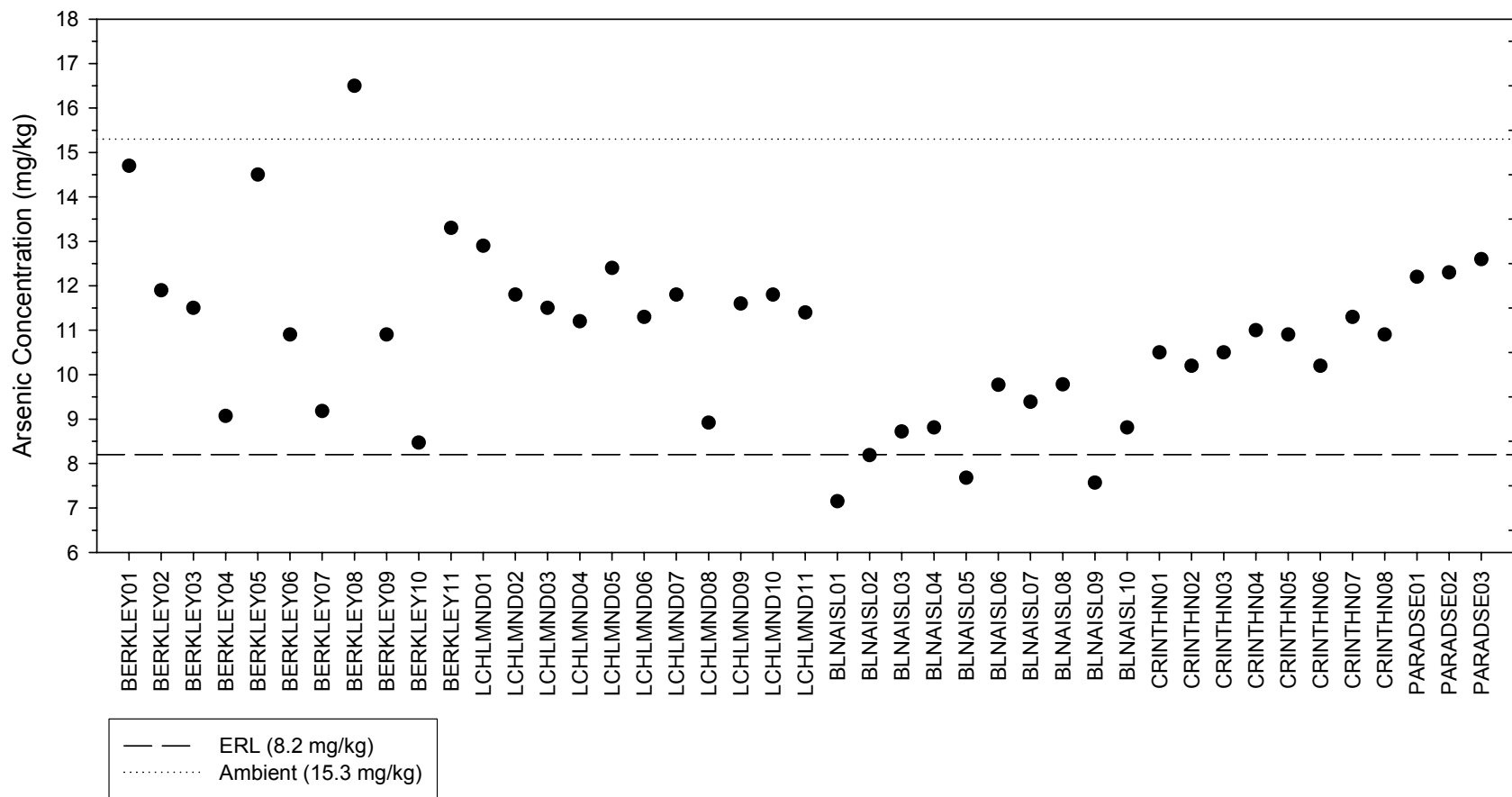


Figure 9. Sediment arsenic concentrations in the marinas and reference site.

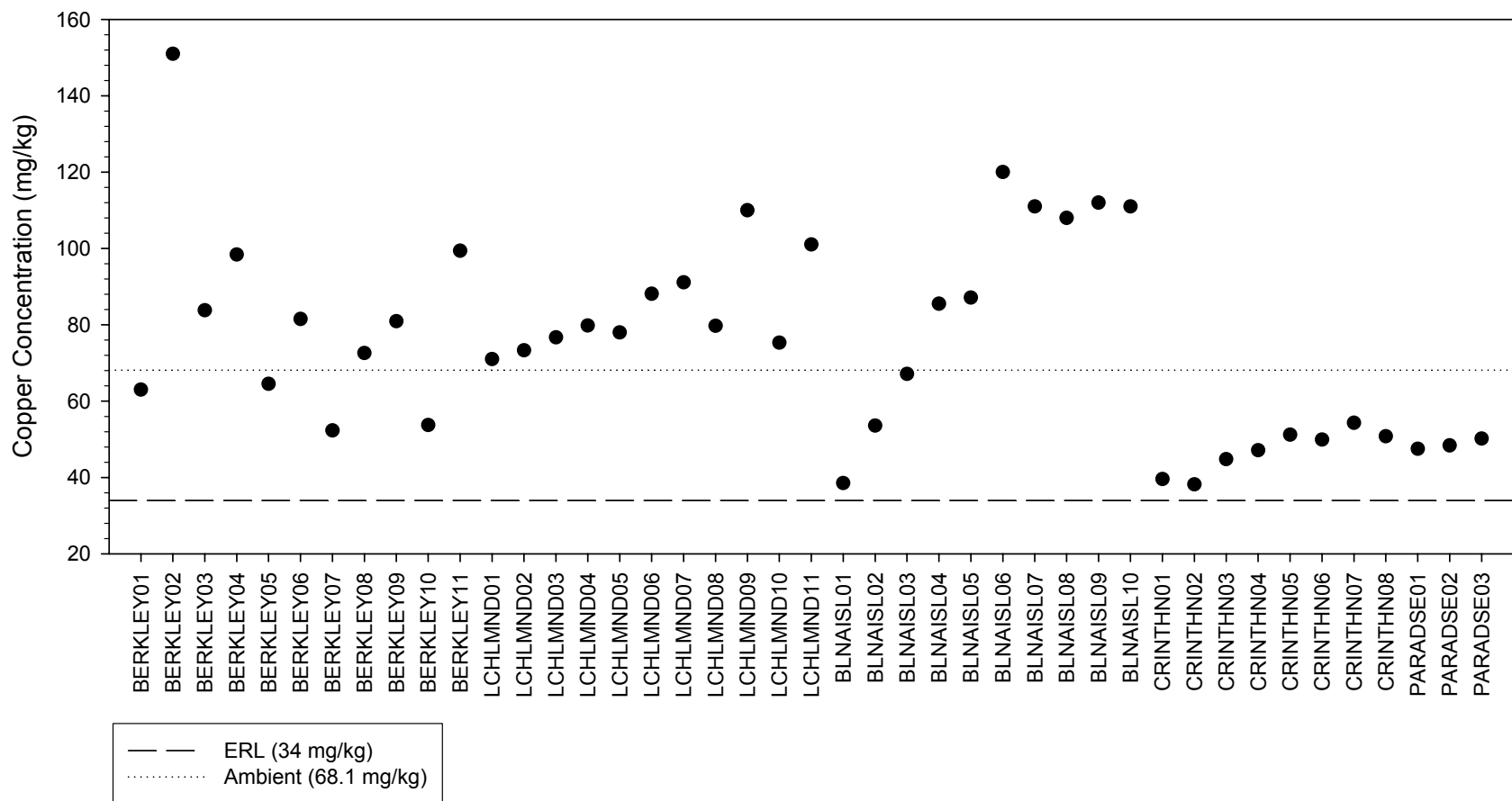


Figure 10. Sediment copper concentrations in the marinas and reference site.

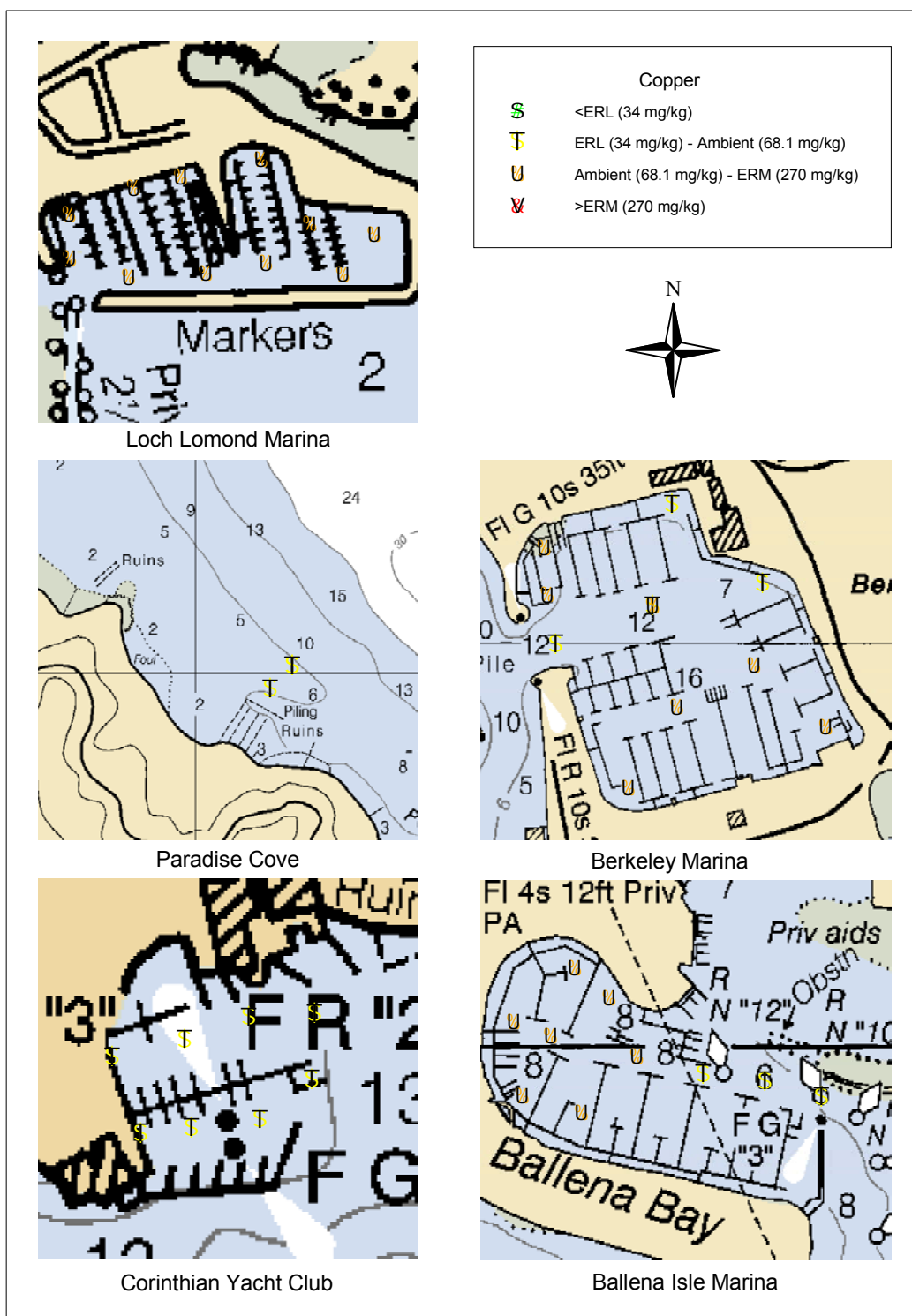


Figure 11. Map displaying distribution of copper concentrations relative to sediment quality guideline thresholds.

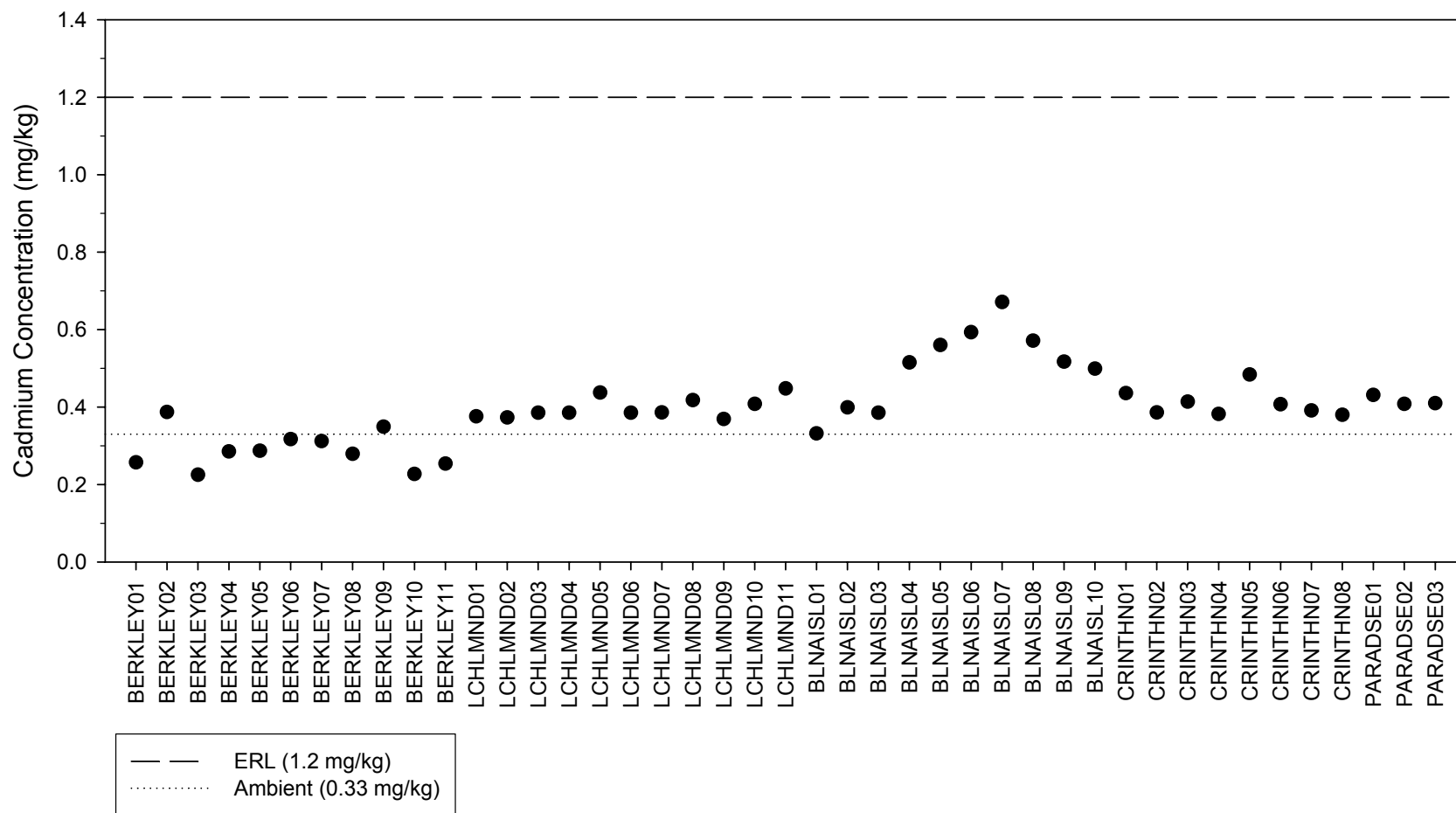


Figure 12. Sediment cadmium concentrations at the marinas and reference site.

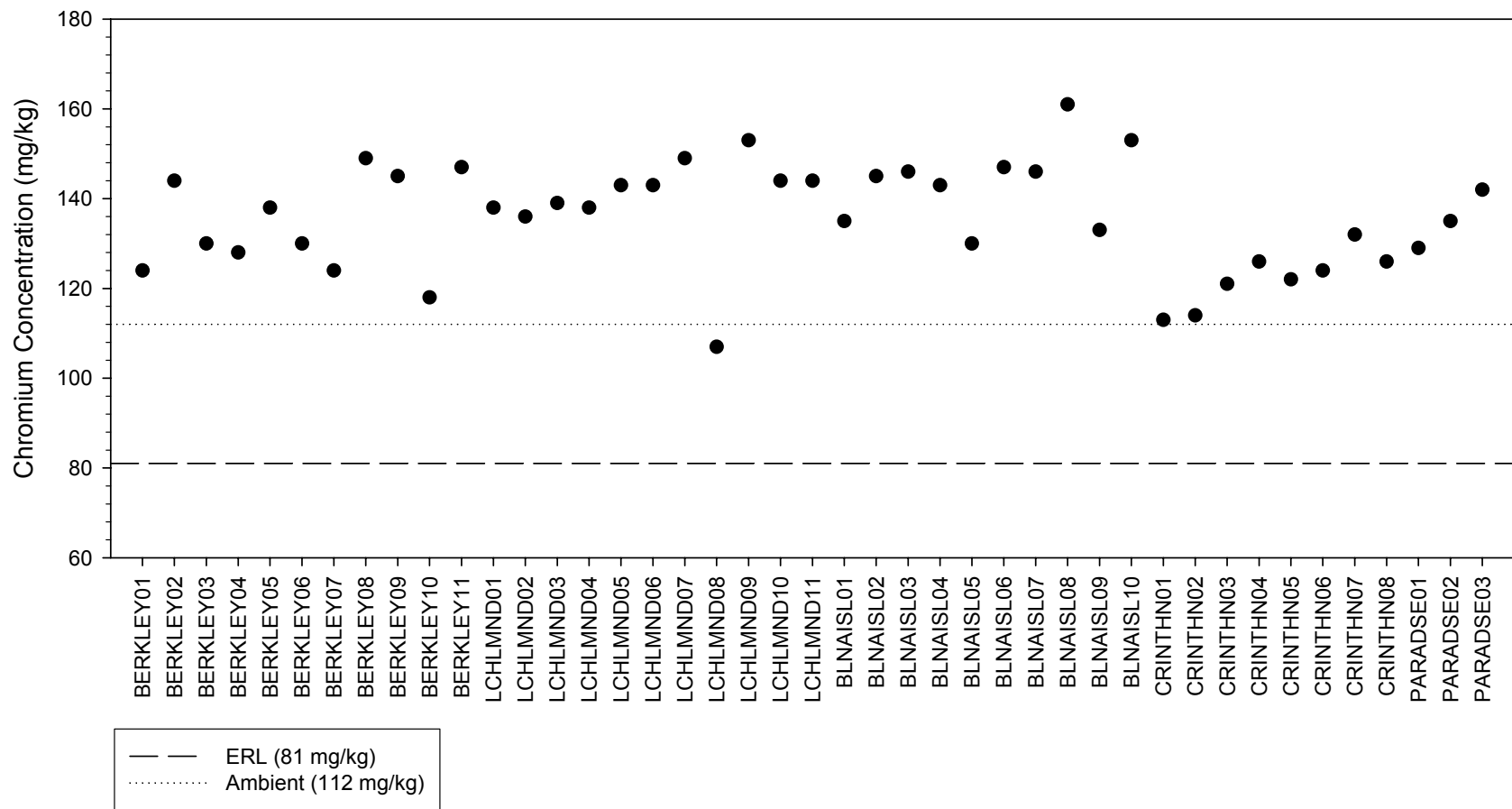


Figure 13. Sediment chromium concentrations at the marinas and reference site.

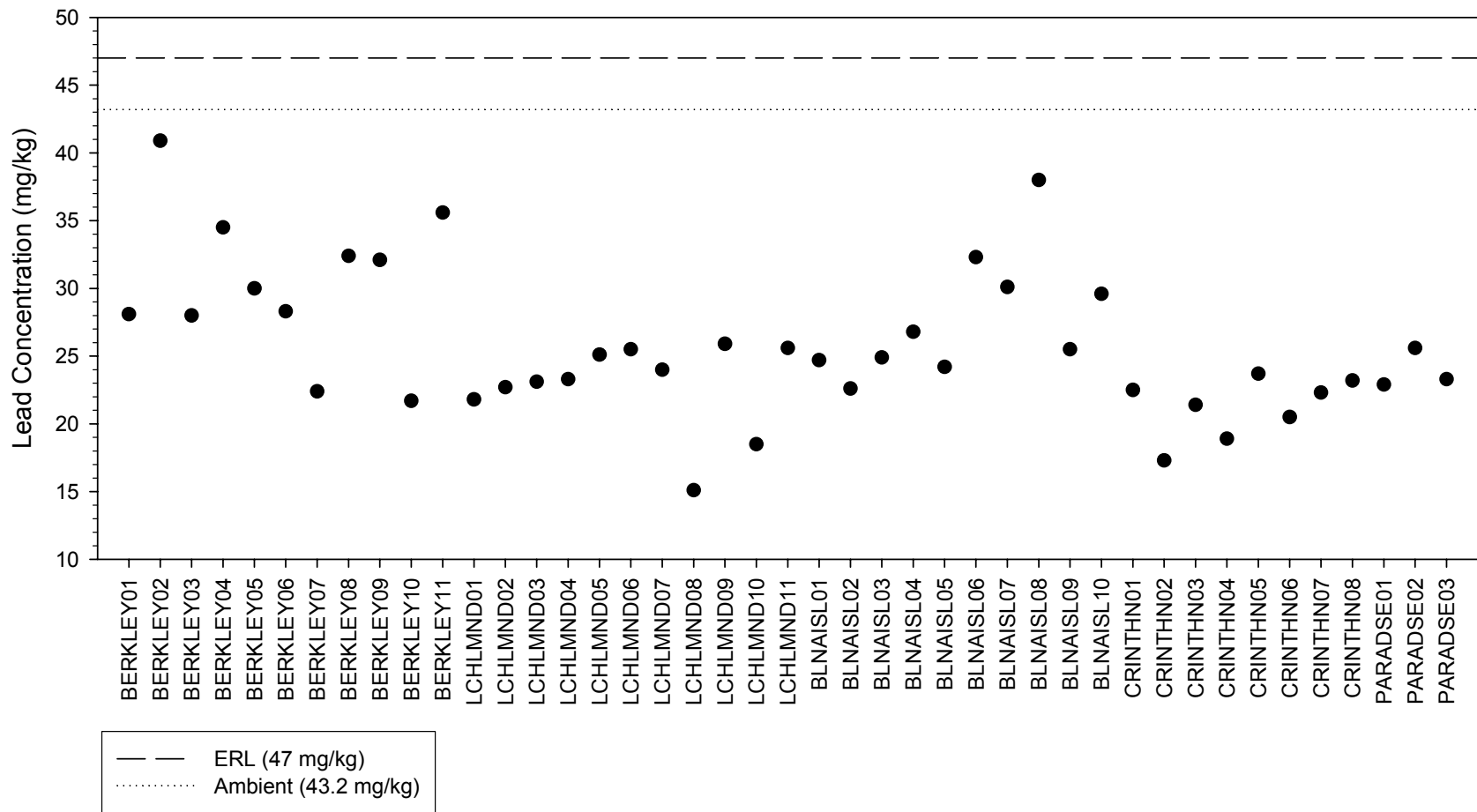


Figure 14. Sediment lead concentrations at the marinas and reference site.

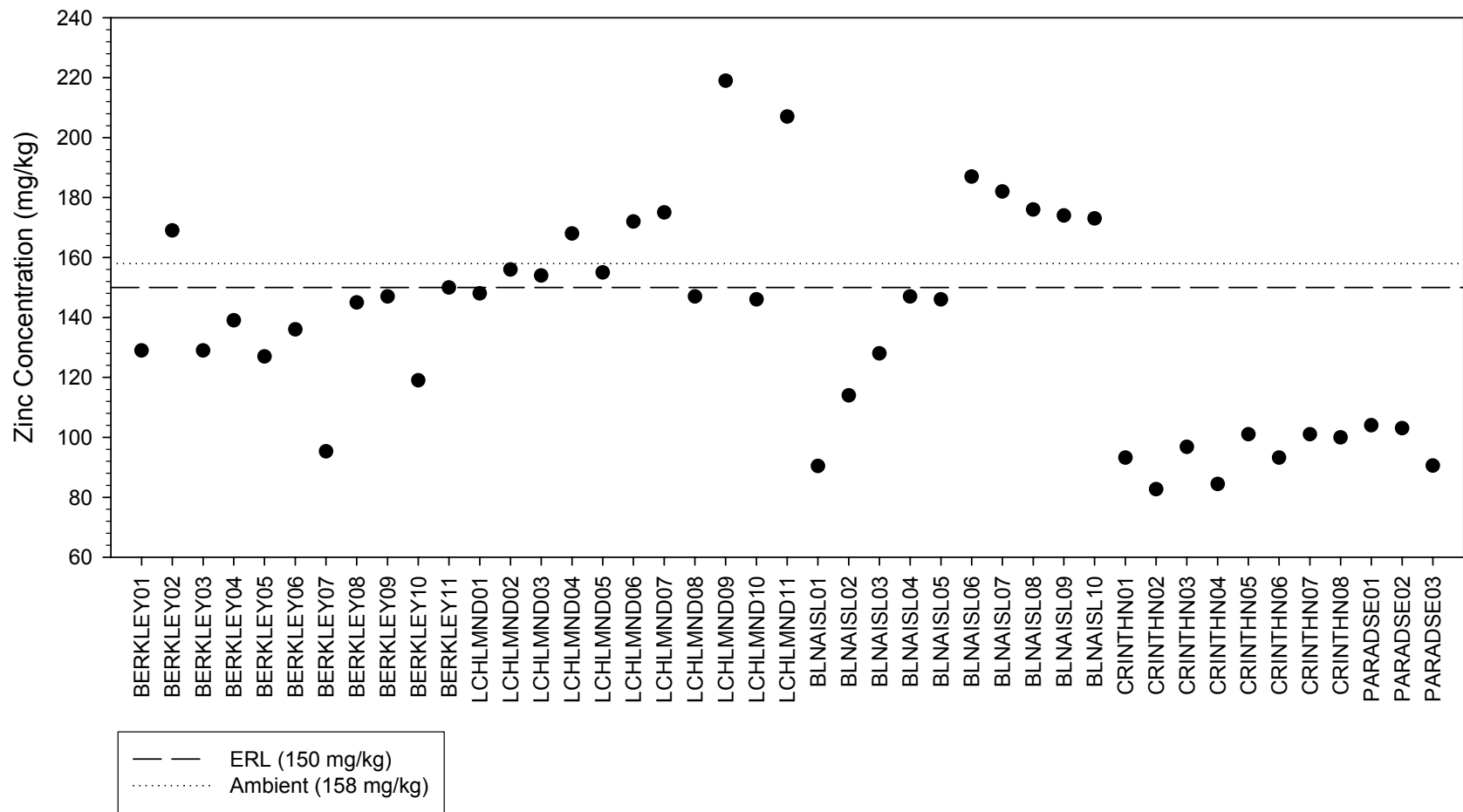


Figure 15. Sediment zinc concentrations at the marinas and reference site.

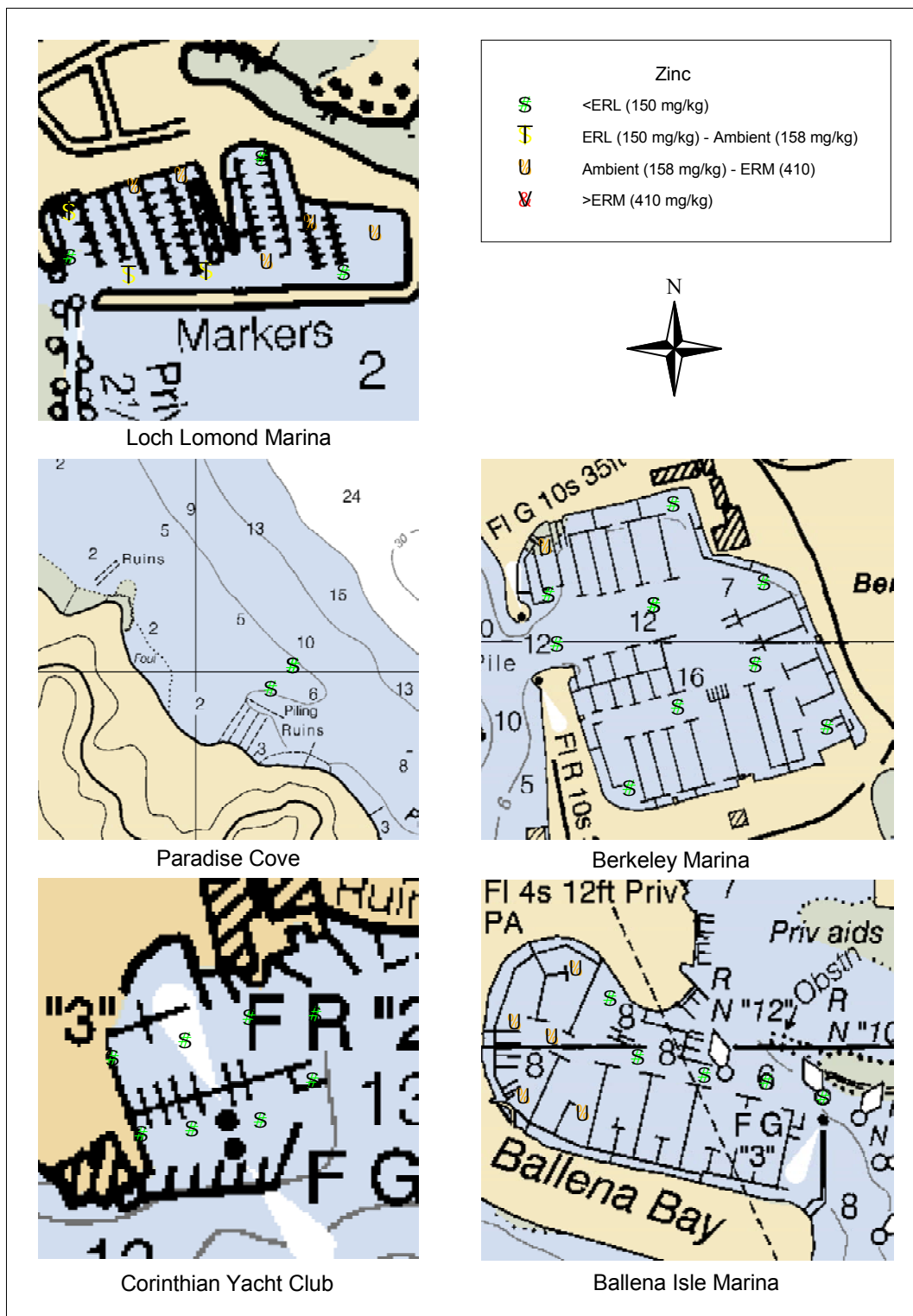


Figure 16. Sampling location maps displaying distribution of zinc concentrations relative to sediment quality guideline thresholds.

Trace Organics (PAHs)

Polycyclic (polynuclear) aromatic hydrocarbons (PAHs) are base/neutral organic compounds with a fused ring structure of two or more benzene rings. Polycyclic aromatic hydrocarbons are formed by the incomplete combustion of coal, oil, petrol, wood, tobacco, charbroiled meats, garbage, or other organic materials. Potential marina and boating related sources of PAHs include fuel and oil spills from fueling and maintenance activities, oily bilge discharges, and releases from older carbureted two-stroke engines (unburned fuel and exhaust). Exposure to PAHs may result in a wide range of carcinogenic, teratogenic and mutagenic effects to terrestrial and aquatic organisms (Eisler, 1987). Due to their similar modes of toxic action, individual PAHs are often grouped into low and high molecular weight compounds, for concise reporting purposes. Individual PAHs used for the summations of low molecular weight PAHs (LMW_PAH) are acenaphthene, acenaphthylene, anthracene, fluorene, naphthalene and phenanthrene. Individual PAHs used for the summations of high molecular weight PAHs (HMW_PAH) are benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, fluoranthene and pyrene. Total PAHs (TTL_PAH) are based on the summation of low and high molecular weight PAHs. Total PAHs were normalized to organic carbon (TOC) to allow comparison to consensus sediment quality guidelines that are based on EqP theory and therefore dependent on OC normalized PAH concentrations from the marina samples. Each of these summations is based on the recommendations of Swartz (1999). Sediment LMW_PAH in the current survey ranged from 111.7 – 1213.3 ng/kg (Figure 17). Sediment HMW_PAH in the current survey ranged from 612.9 – 4081 ng/kg (Figure 18). Sediment TTL_PAH in the current survey ranged from 774.3 – 5294.3 ng/kg (Figure 19). Organic carbon normalized TTT_PAH in the current survey ranged from 57.8 – 326.8 ug/g OC (Figure 20).

Low molecular weight and total PAHs rarely exceeded either the ERL guidelines or Ambient concentrations for San Francisco Bay. Only two stations in Corinthian Yacht Club and one in Ballena Isle Marina demonstrated concentrations above these guideline values. High molecular weight PAHs were slightly more elevated with approximately half exceeding ERL guidelines. Two stations in Berkeley, one in Ballena Isle and two in Corinthian exceeded both the ERL guidelines and the ambient values. Loch Lomond marina exhibited significantly lower PAH concentrations than the other marinas. A single station in Corinthian Yacht Club (CRINTHN05) consistently demonstrated the greatest values for low, high, total and OC normalized PAHs. It is unclear why this one location stands out for PAH contamination, so additional attention may be needed at this location in future surveys.

None of the multiple chemical summations (high, low or total PAHs) exceeded ERM or PEL guidelines for any grouping of PAHs where acute effects would be more probable. Similarly, none of the samples exceeded the organic carbon normalized guideline value (1800ug/g OC) for PAHS (Figure 20), where biological effects would be expected. It is unlikely that the PAH levels in the marina pose a significant risk of acute effects to aquatic life.

PAH distributions are effective interpretive tools in hydrocarbon fingerprinting and can be used to distinguish general sources of hydrocarbons as either pyrogenic or petrogenic. By examining the relative distribution of the C₁, C₂, C₃, and C₄ alkyl homologues of a PAH class (Sauer *et al.*, 1993) and the relative concentrations of the low molecular weight PAHs (e.g.- naphthalene,

fluorene, dibenzothiophene) to the higher molecular weight PAHs (e.g.-fluoranthene, chrysene, benzo(a)pyrene) general sources can be determined (Boehm *et al.*, 1981) Examination of the relative higher abundance of high molecular parent PAHS indicates that PAHs in the marina samples PAHs have a pyrogenic signature, most likely from the combustion of fuel. Further review of the C₁ - C₄ homologues for naphthalene, chrysene, and phenanthrene/anthracene further support a pyrogenic source, but also show some indications of a petrogenic signal, which is likely uncombusted fuel. This pattern is consistent throughout the marinas so it seems plausible to infer that PAHs in marina sediments are primarily from combusted fuel, but do show some further indications of unburned fuel. Minor fuel or oils spills or bilge pumping may be possible suspects for the source of unburned fuel though additional fingerprinting research would be required to fully investigate sources.

In summary, PAH compounds are currently detectable in the marinas though not at concentrations that present a high probability of acute toxicity. The PAHs present are primarily from burned fuel with some minor indications of spilled fuel also being present.

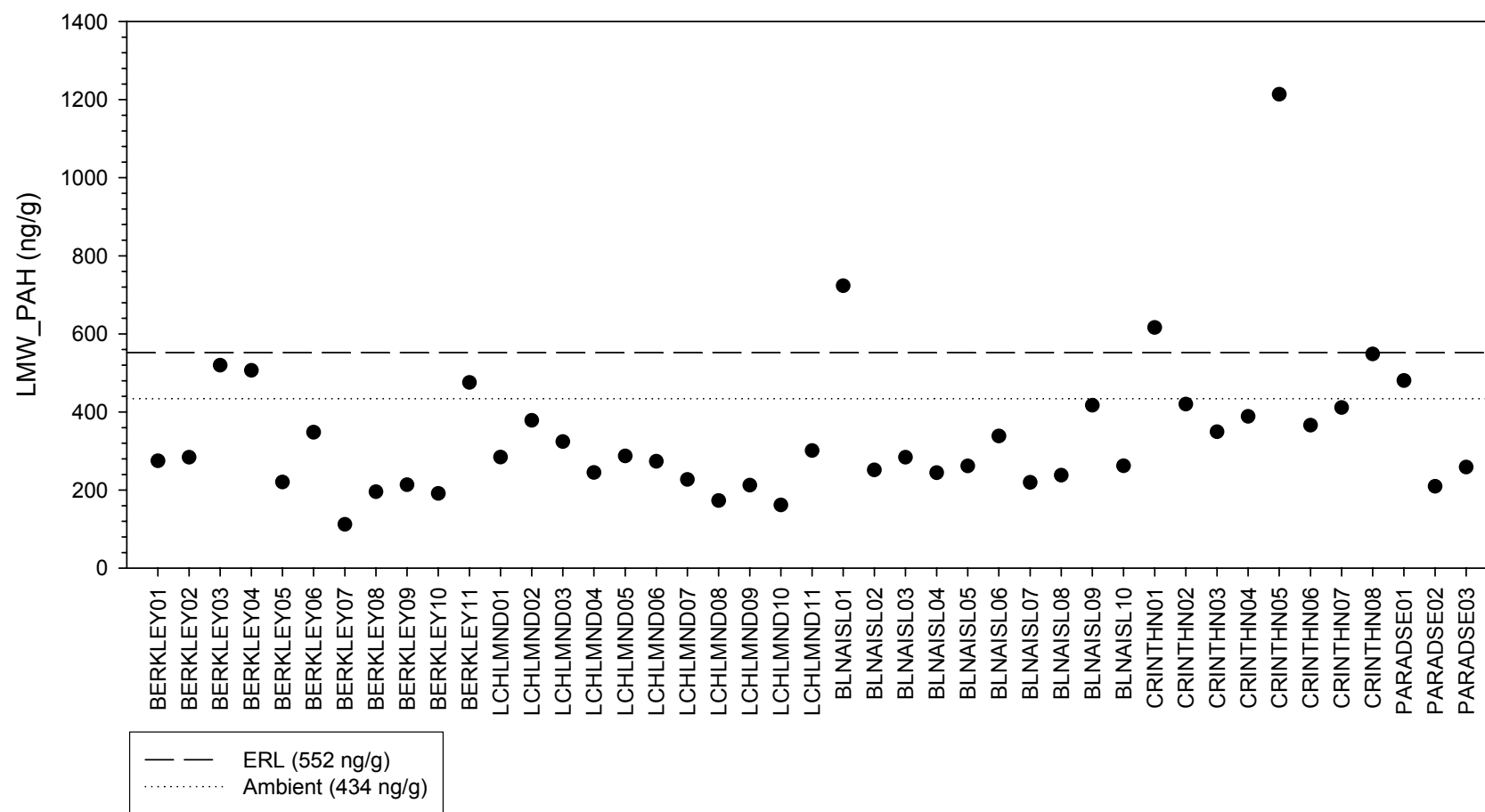


Figure 17. Histogram of Low Molecular Weight PAHs (LMW_PAH) in the marinas and reference site.

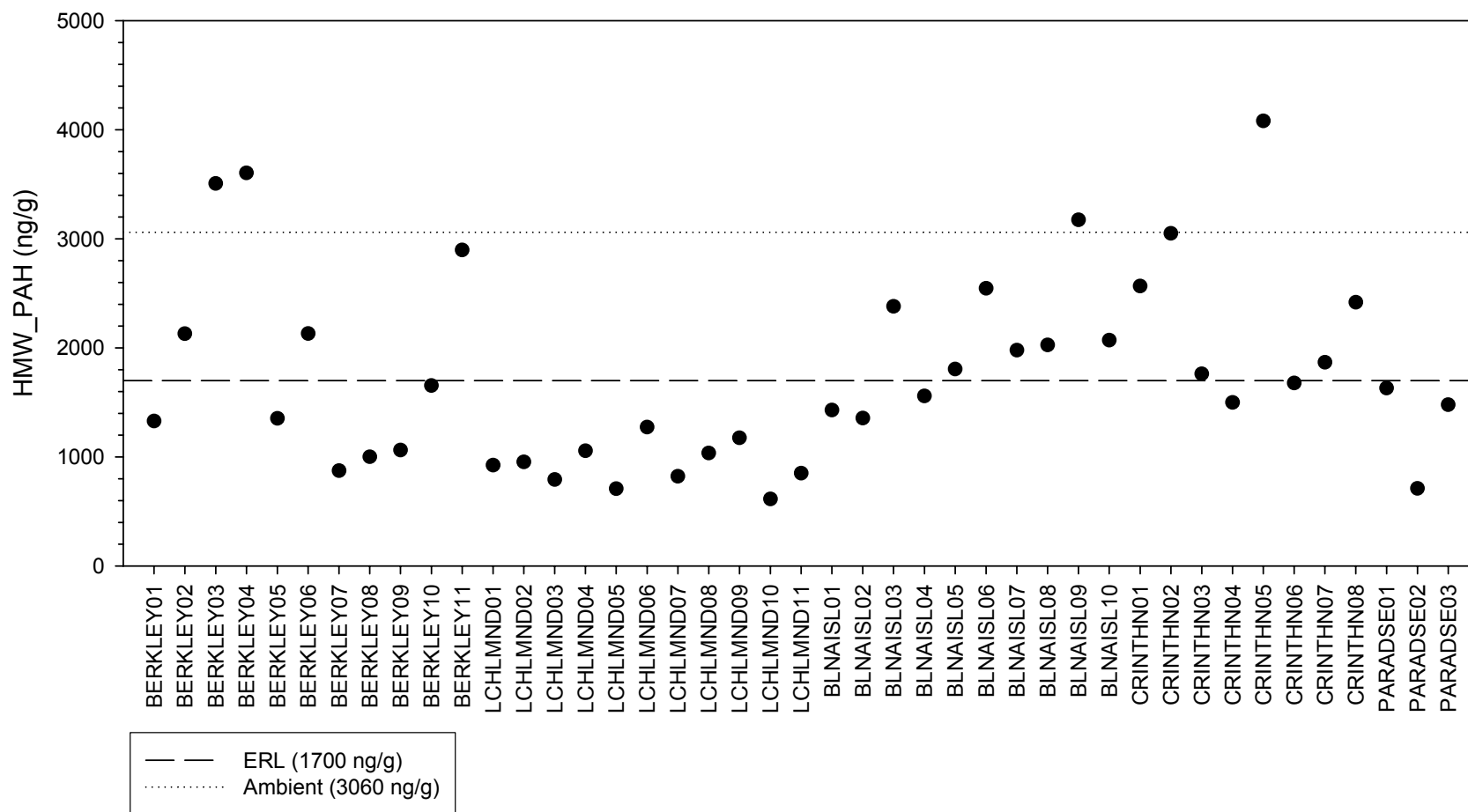


Figure 18. Histogram of High Molecular Weight PAHs (HMW_PAH) in the marinas and reference site.

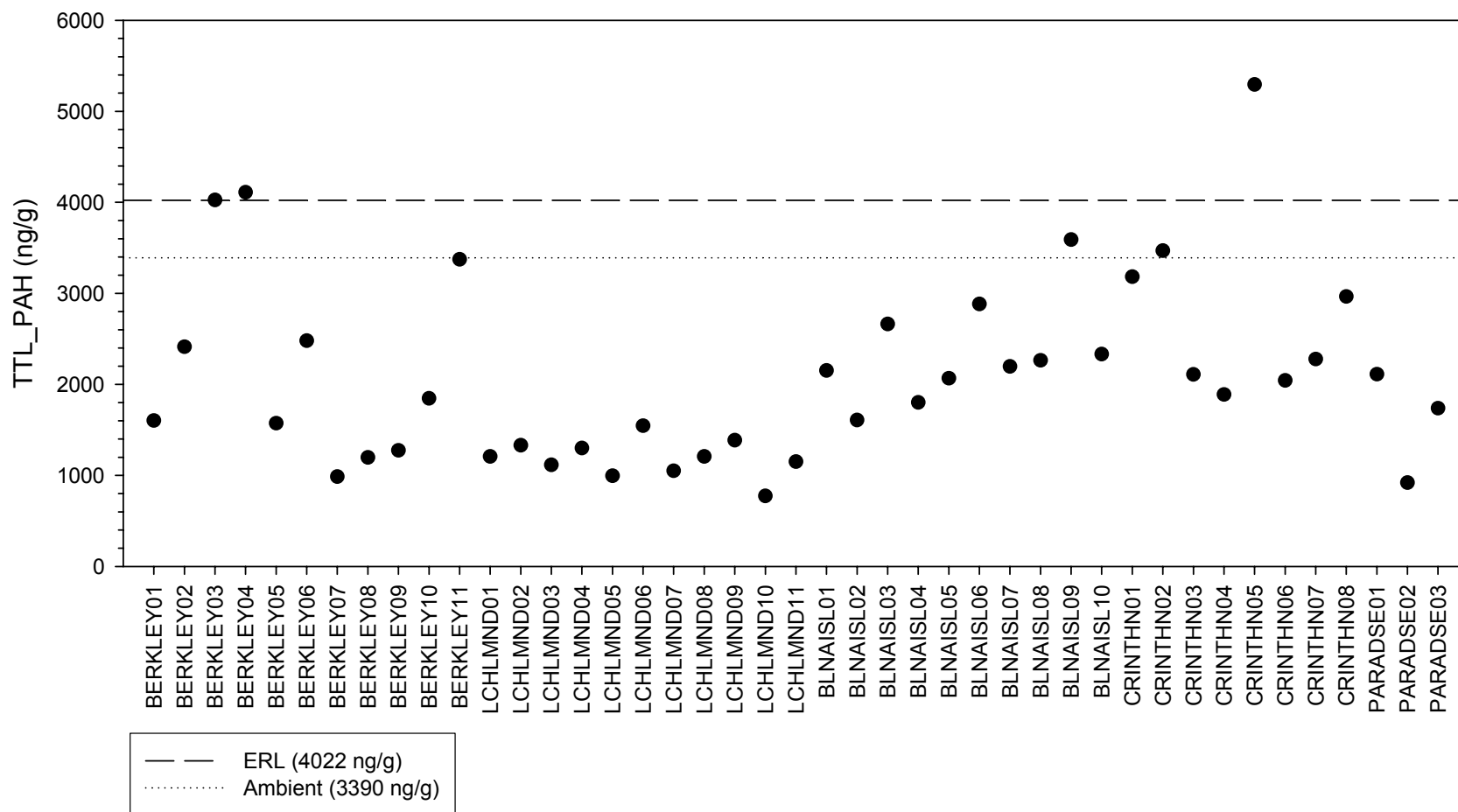


Figure 19. Histogram of Total PAHs (TTL_PAH) in the marinas and reference site.

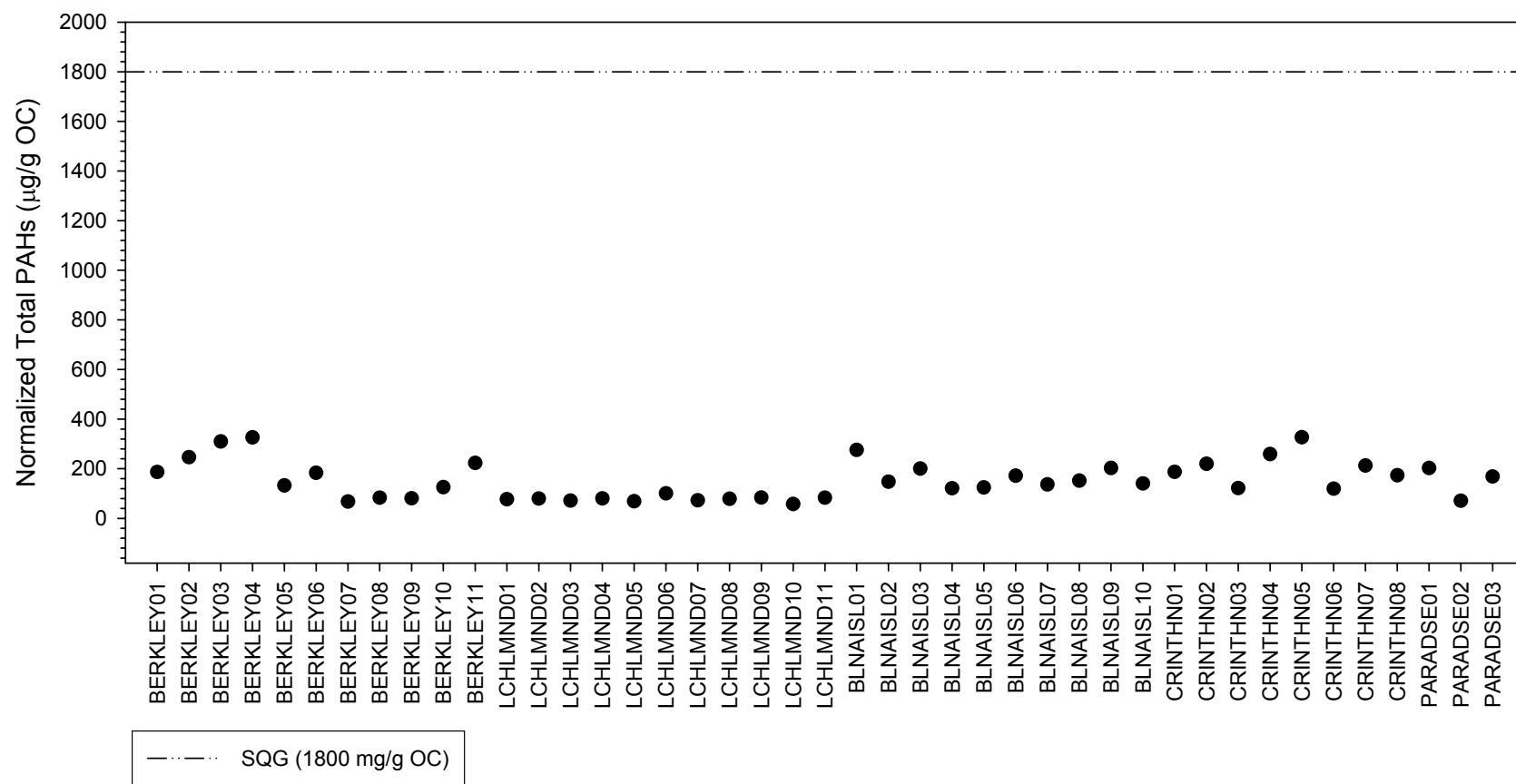


Figure 20. Histogram of Total PAHs normalized to Total Organic Carbon (TOC) in the marinas and reference site.

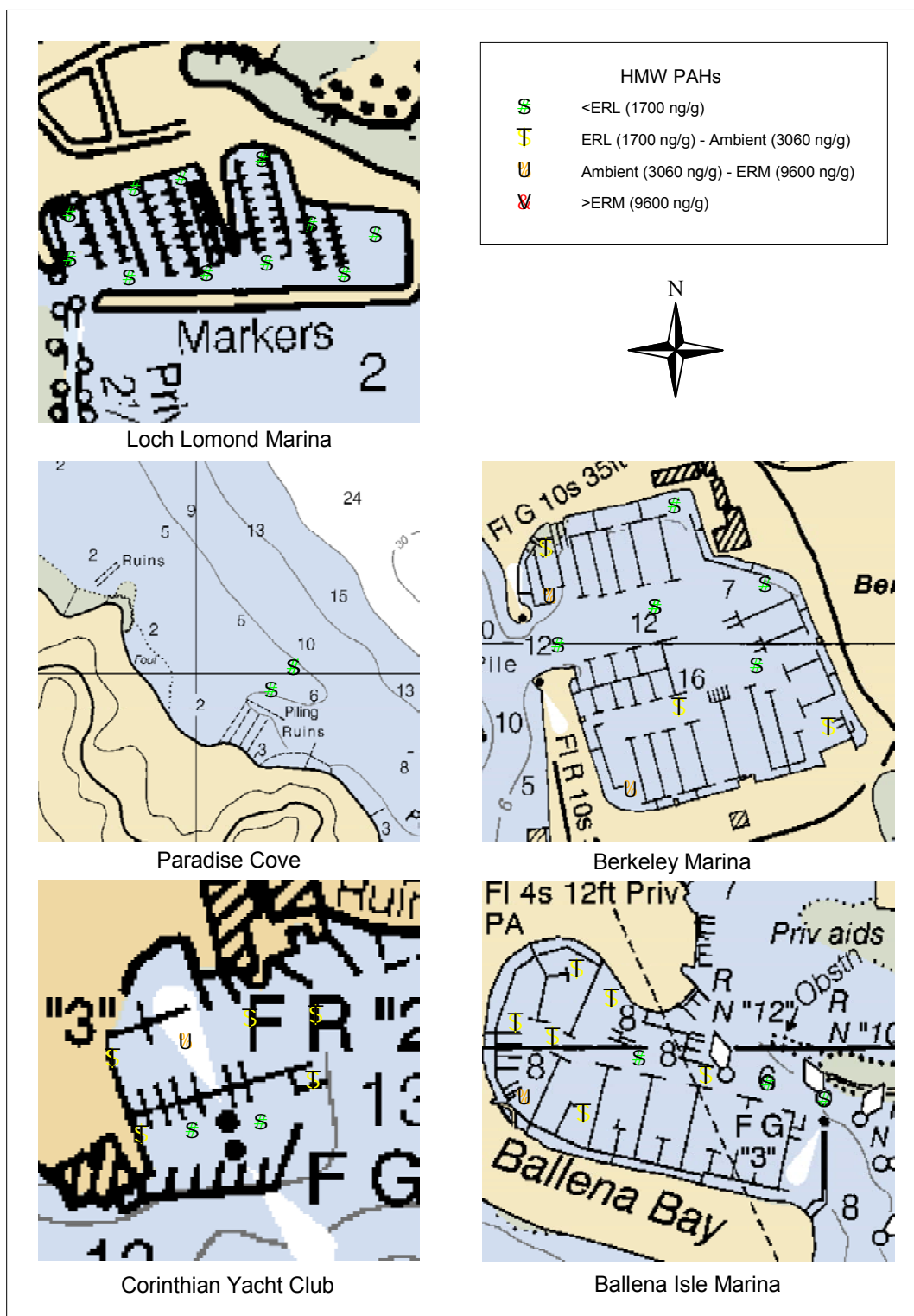


Figure 21. Map displaying distribution of HMW PAH concentrations relative to sediment quality guideline thresholds.

Statistical Analyses

Sediment concentration significantly differed for each metal across all marinas (Table 4). Pairwise comparisons indicate Berkeley and Corinthian Yacht Club were not significantly different than Paradise Cove reference station for each metal (Table 4). Furthermore, Loch Lomond only had one significant difference (zinc) with Paradise Cove. These results could be an artifact of location in that Corinthian Yacht Club, Paradise Cove, and Loch Lomond are on the same side of the Bay. However, it is interesting to note that Loch Lomond and Corinthian Yacht Club had the most significant differences ($n=7$). A clear pattern did not exist between Berkeley, Loch Lomond, and Ballena Isle. In terms of each metal, zinc had the highest number of significant correlations with other metals (cadmium, chromium, copper, and lead), PAHs (LMW and normalized total), % fines, and % TOC (Table 5). Chromium also appears to have a high number of positive associations with other analytes (copper, % fines, lead, zinc, and LMW PAHs). While most of the metals had a positive association (i.e., both tending to increase in concentration), arsenic and cadmium had a negative correlation in which cadmium concentration decreased as arsenic concentration increased.

Sediment concentration of LMW, HMW, total, and normalized total PAHs significantly differed across all marinas (Table 4). Loch Lomond marina had significantly lower sediment concentrations of HMW, total, and normalized total PAHs compared to Berkeley, Ballena Isle, and Corinthian Yacht Club, where LMW PAHs also significantly differed, but showed no significant differences with Paradise Cove reference station (Table 4). Other pairwise comparisons between the marinas showed no significant differences. All of the PAHs (i.e., LMW, HMW, total, and normalized total) were correlated and showed a positive relationship (Table 5).

Anova comparisons of chemicals indicated numerous significant chemical specific differences between the various harbors (Table 4). In some cases a particular marina exhibited significantly lower concentrations of one chemical while also exhibited significantly greater concentrations of another. One example is that arsenic concentrations were significantly lower in Ballena Isle marina than other marinas, yet copper concentrations were significantly greater there than seen at Corinthian and at the Paradise Cove reference stations. Another example is that zinc was significantly higher in Loch Lomond than all marinas except Ballena Isle. Although differences are evident, overall there was no clear pattern of differences in metal concentrations between Berkeley, and Ballena Isle Marinas. Specific differences of note are: 1) Corinthian Yacht Club tended to have significantly lower metal concentrations than all other marinas, which is further supported by the observation that no statistical differences could be discerned between Corinthian Yacht Club and the nearby reference site at Paradise Cove; 2) Loch Lomond tended to have significantly lower PAH concentrations than most other marinas, though zinc was significantly greater there; 3) TOC and grain size showed no significant differences among the harbors, 4) Zinc was the metal most often seen to have differences between harbors.

Specific chemical correlations were performed to investigate whether any common patterns in use or sources could be discerned (Table 5). As expected, all the PAHs tended to be correlated with each other and suggest a common source. Earlier discussion of PAHs indicated that burned

fuel is the most likely explanation. PAHs were generally not correlated or were negatively correlated with metals, so their use or sources do not seem to strongly linked. Copper, cadmium and zinc were often positively correlated suggesting common uses (such as bottom paints) might be the source of these metals to the marinas. Arsenic however did not correlate or was negatively correlated with the other metals indicating a separate use or source (such as wood preservatives). Zinc was positively correlated with all the metals, except arsenic, and also positively correlated with TOC and grain size. Interestingly, zinc was the only chemical positively correlated with lead. These relationships, in concert with the strong differences in zinc concentrations between harbors provide a complex picture for use and sources of zinc that cannot easily be discerned from this study. Zinc in the marina sediments may result from multiple uses or sources.

Table 5. Results for the statistical comparison of analyte concentrations across all marinas and among marinas. A ‘Yes’ value indicates a significant difference according to either a parametric One Way Analysis of Variance (ANOVA) or a non-parametric Kruskal-Wallis One Way ANOVA. If a significant difference was present, the test statistic, test value, degrees of freedom (df), and p value are listed.

Comparison	Arsenic	Cadmium	Chromium	Copper	Lead	Zinc	% Fines	% TOC	LMW PAH	HMW PAH	TTL PAH	nTTL PAH
All Harbors	Yes (KW, H=23.35, df=4, p<0.01)	Yes (KW, H=25.10, df=4, p<0.01)	Yes (AN, F=5.87, df=4, p<0.01)	Yes (AN, F=6.75, df=4, p<0.01)	Yes (AN, F=7.88, df=4, p<0.01)	Yes (AN, F=15.40, df=4, p<0.01)	No	No	Yes (KW, H=11.72, df=4, p=0.02)	Yes (AN, F=6.29, df=4, p<0.01)	Yes (AN, F=5.94, df=4, p<0.01)	Yes (KW, H=19.13, df=4, p<0.01)
Berkeley & Loch Lomond	No	No	No	No	Yes (T, q=6.02, p<0.01)	Yes (T, q=4.80, p=0.01)			No	Yes (T, q=4.87, p=0.01)	Yes (T, q=4.33, p=0.03)	Yes (D, Q=3.26, p<0.05)
Berkeley & Ballena Isle	Yes (D, Q=3.62, p<0.05)	Yes (D, Q=4.77, p<0.05)	No	No	No	No			No	No	No	No
Berkeley & Corinthian Yacht Club	No	No	No	Yes (T, q=5.08, p=0.01)	Yes (T, q=6.66, p<0.01)	Yes (T, q=5.49, p<0.01)			No	No	No	No
Berkeley & Paradise Cove	No	No	No	No	No	No			No	No	No	No
Loch Lomond & Ballena Isle	Yes (D, Q=3.96, p<0.05)	No	No	No	No	No			No	Yes (T, q=5.09, p=0.01)	Yes (T, q=4.60, p=0.02)	Yes (D, Q=3.27, p<0.05)
Loch Lomond & Corinthian Yacht Club	No	No	Yes (T, q=5.29, p=0.01)	Yes (T, q=5.38, p<0.01)	No	Yes (T, q=9.90, p<0.01)			Yes (D, Q=3.18, p<0.05)	Yes (T, q=6.23, p<0.01)	Yes (T, q=6.36, p<0.01)	Yes (D, Q=3.85, p<0.05)
Loch Lomond & Paradise Cove	No	No	No	No	No	Yes (T, q=6.57, p<0.01)			No	No	No	No
Ballena Isle & Corinthian Yacht Club	No	No	Yes (T, q=6.53, p<0.01)	Yes (T, q=6.04, p=0.01)	Yes (T, q=4.75, p=0.02)	Yes (T, q=7.57, p<0.01)			No	No	No	No
Ballena Isle & Paradise Cove	Yes (D, Q=3.55, p<0.05)	No	No	Yes (T, q=4.18, p=0.04)	No	Yes (T, q=4.97, p=0.01)			No	No	No	No
Corinthian Yacht Club & Paradise Cove	No	No	No	No	No	No			No	No	No	No

AN = One Way Analysis of Variance (ANOVA), D = Dunn's Pairwise Multiple Comparison, KW = Kruskal-Wallis One Way ANOVA on ranks, T = Tukey Pairwise Multiple Comparison

Table 6. Results for the analyte comparisons with the Pearson Product Moment Correlation (r). A positive r value indicates a direct relationship while a negative value indicates an inverse relationship. Sample size is 43 for each comparison.

	Arsenic	Cadmium	Chromium	Copper	% Fines	Lead	% TOC	Zinc	LMW PAH	HMW PAH	TTL PAH	nTTL PAH
Arsenic	*	Yes (r=-0.41, p=0.01)	No	No	No	No	No	No	No	No	No	No
Cadmium		*	No	Yes (r=0.32, p=0.04)	No	No	Yes (r=0.36, p=0.02)	Yes (r=0.31, p=0.04)	No	No	No	No
Chromium			*	Yes (r=0.59, p<0.01)	Yes (r=0.38, p=0.01)	Yes (r=0.58, p<0.01)	No	Yes (r=0.65, p<0.01)	Yes (r=-0.34, p=0.02)	No	No	No
Copper				*	Yes (r=0.33, p=0.03)	Yes (r=0.67, p<0.01)	No	Yes (r=0.87, p<0.01)	No	No	No	No
% Fines					*	No	No	Yes (r=0.32, p=0.04)	No	No	No	No
Lead						*	No	Yes (r=0.45, p<0.01)	No	No	No	No
% TOC							*	Yes (r=0.35, p=0.02)	No	No	No	Yes (r=-0.40, p=0.01)
Zinc								*	Yes (r=-0.37, p=0.01)	No	No	Yes (r=-0.37, p=0.02)
LMW PAHs									*	Yes (r=0.67, p<0.01)	Yes (r=0.77, p<0.01)	Yes (r=0.72, p<0.01)
HMW PAHs										*	Yes (r=0.99, p<0.01)	Yes (r=0.83, p<0.01)
TTL PAHs											*	Yes (r=0.86, p<0.01)
nTTL PAHs												*

LIMITATIONS

It is important to note that the current study was not a comprehensive monitoring effort designed for targeting a wide range of anthropogenic contaminants. Due to funding constraints, the specific pollutants targeted (five metals and PAHs) were identified as those most likely related to boating activities within the marina. There are a substantial number of other pollutants, related to other activities, which may be present in the marinas that this survey has not considered. Examples are industrial and agricultural compounds such as PCBs, phthalates, nutrients, pesticides, fungicides and estrogenic compounds that may enter the marinas through runoff, leaching, stormwater drains or other sources. Effects from unmeasured pollutants should not be implied here, but neither should the potential impacts of other chemicals be overlooked based on the findings of the survey. The marinas that were studied for this survey were selected based on criteria that minimized inputs from many of the outside sources, relative to other San Francisco Bay marinas. From that bias it should become clear that other unmeasured pollutants may pose an even greater probability of biological risk within the other marinas.

It should also be made clear that extrapolation of the results presented here to the numerous other marinas of San Francisco Bay must be made with caution. Although selection criteria were carefully considered in choosing the four marinas surveyed, not all marinas fit the selection criteria in the same ways with respect to size, use and potential sources of contamination. Each likely present its own unique chemical signature based on the conditions and activities that are found there. For example, different water flushing rates and patterns may contribute to differences in contaminant levels found in each marina. For these reasons, the reader is cautioned from drawing definitive conclusions on the differences between the marinas surveyed and whether one marina “worse” or “better” than another in terms of controlling pollution. The four marinas surveyed here do however encompass a broad range of conditions and activities commonly found in most marinas, so have been good representatives for this pilot study to help establish chemical ranges and probabilities of biological impacts.

The sediment quality guidelines used in this report for chemical comparisons were primarily developed based on short term (10 day) acute exposures of amphipods to field collected sediments. Chronic toxicity test, bioaccumulation or community indices that better integrate more sensitive species and long term exposure have not been well incorporated into the guideline development. The purpose of the incidental collection of benthic community samples was to allow some biological assessment of chronic exposure to marina contaminants. Until funding is secured to analyze those communities few informed statements can be made about community health. It is therefore prudent to caution that the sediments in the marinas have not been appropriately investigated for effects resulting from chronic exposure to pollutants.

SUMMARY OF RESULTS

1. Sediment quality guidelines were useful in evaluating chemical pollution within the sediments of four San Francisco Bay marinas. Arsenic, chromium, copper, and zinc were most often found to exceed established Effects Range Low (ERL), Threshold Effects Levels (TEL) and Ambient guideline values. Use of these guidelines indicates that these chemicals pose a low, to occasionally moderate, probability of having associated acute toxic effects to aquatic life. Of these four metals, copper and chromium are of greatest concern. Long-term status and trend monitoring of these four trace metals in marinas is recommended.
2. Dissolved oxygen concentrations in Ballena Isle and Berkeley Marinas were low (<4 mg/l) in bottom waters at several locations and may present a risk of hypoxia to aquatic life. Additional monitoring of oxygen levels is recommended to improve both spatial and temporal resolution of oxygen saturation conditions.
3. Measured concentrations of cadmium, lead and polycyclic aromatic hydrocarbons (PAHs) were generally low and pose a low probability of having associated acute toxic effects to aquatic life.
4. Statistical analyses indicate Corinthian Yacht Club tended to have significantly lower metal concentrations than all other marinas, and was similar to the reference site at Paradise Cove. There was no clear pattern of statistical differences in metal or PAH concentrations among Berkeley, and Ballena Isle Marinas. Loch Lomond tended to have significantly lower PAH concentrations than most other marinas, though zinc was significantly greater there. Zinc was the metal most often seen to have differences between harbors while TOC and grain size showed no significant differences among the harbors.
5. PAHs were generally not correlated or were negatively correlated with metals, so their use or sources do not seem to be strongly linked. Copper, cadmium and zinc were often positively correlated suggesting common uses, such as bottom paints, might be the source of these metals to the marinas. Arsenic did not correlate or was negatively correlated with the other metals indicating a separate use or source, possibly treated wood products.

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